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RPPR Final Report
as of 31-Oct-2018

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Proposal Number: 62336MS **Agreement Number: W911NF-12-1-0545**

INVESTIGATOR(S):

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Final Report for Period Beginning 15-Sep-2012 and Ending 14-Sep-2016
Title: Self-Assembled Multiferroic Nanostructures and Studies on Magnetoelectric Interactions (Research Area: 10.1)
Begin Performance Period: 15-Sep-2012 **End Performance Period:** 14-Sep-2016
Report Term: 0-Other
Submitted By: Gopalan Srinivasan Email: srinivas@oakland.edu
Phone: (248) 370-3419
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 10 **STEM Participants:** 8

Major Goals: Major Goals
Ferromagnetic–ferroelectric composites show strong magneto-electric (ME) coupling at room temperature that is mediated by mechanical forces. The focus of the proposed effort was on ME interactions in core-shell nanoparticles and nanowires of ferrite-piezoelectrics. The large surface area-to-volume ratio for the nano-composites is expected to lead to a much stronger ME interactions compared to bulk materials. We modeled ME interactions in nanobilayers, nanopillars and nanotubes comprising a ferroelectric phase and a ferromagnetic phase. The model for low frequency ME coupling predicted a substantial reduction in ME coefficients in nano-bilayers on a substrate due to substrate clamping, but the clamping effects can be substantially reduced in core-shell particles and coaxial wires. The important inferences from the models were the prediction of strong ME coupling at low-frequencies and at resonance modes in nanocomposites and the potential for novel devices based on the phenomena for high frequency electronics.
The key objectives were to synthesize nano-composites and assemble them into superstructures which were predicted to exhibit strong ME effects. The ME were to be assembled into composites with different connectivity schemes, such as core-shell nanoparticles (0-0) and coaxial nanofibers (1-1). Self-assembly techniques to be employed were chemical and electric and magnetic field assisted assembly.
Planned tasks included the following:

- Synthesis of composites of 0-D core-shell particles and 1-D coaxial wires with nickel zinc ferrite for the ferromagnetic phase and ferroelectric PZT or barium titanate;
- Assemble the building blocks by chemical self-assembly, DNA-assisted assembly or electric or magnetic field assisted assembly into superstructures of rings, chains, 2D and 3D periodic arrays;
- Studies on low-frequency and resonance ME effects;
- Modeling efforts for correlation between material processing, composition, connectivity scheme, self-assembly parameters, and ME properties; and
- Explore the use of nanostructures for high frequency electronics.

Accomplishments: Accomplishments
Studies were carried out on two types of ferrite-ferroelectric nano-composites: core-shell particles and coaxial nanowires. Key accomplishments of our efforts included the following.
(i) Chemical self-assembly of 10-400 nm nickel ferrite and 50-600 nm barium titanate core-shell nano-particles by click-reaction followed by field directed assembly.
(ii) Core-shell particles by DNA/RNA-assisted assembly;
(iii) Synthesis of ferrite-ferroelectric core-shell nanowires by electro-spinning and assembly in uniform or non-

uniform magnetic fields.
(iv) Observation of strong low-frequency ME coupling and millimeter wave magneto-dielectric effects in the nanostructures.
(v) First principles theory of low-frequency ME effects, magneto-dielectric effects and H-assisted assembly.

1. Synthesis of core-shell nanoparticles by chemical assembly, magnetic field assisted assembly into superstructures and studies on ME interactions:
(a) Chemical self-assembly of core-shell particles: We synthesized core-shell multiferroic nano-composites by functionalizing 10-100 nm barium titanate (BTO) and nickel ferrite (NFO) nanoparticles with complementary coupling groups and allowing them to self-assemble in the presence of a catalyst. The core-shell structure was confirmed by electron microscopy and magnetic force microscopy. Evidence for strong strain mediated magneto-electric coupling was obtained by static magnetic field induced variations in the permittivity over 16-18 GHz and polarization and by electric field induced by low-frequency ac magnetic fields. – Applied Physics Letter 104, 052901 (2014)

(b) Magnetic field assembly of core-shell particles: Linear chains and arrays of chemically self-assembled core-shell nanoparticles of nickel ferrite and barium titanate have been obtained by magnetic-field-assisted assembly (MFAA). Studies on strain mediated ME effects by ME voltage coefficient (MEVC) measurements reveal higher MEVC for MFAA samples than for unassembled films and is higher for magnetic fields parallel to the array orientation than for transverse fields. The strongest ME effect was measured in MFAA-films with a maximum MEVC of 8 mV/cm Oe, one of the highest reported for as-assembled nanocomposite. A model was discussed for the ME coupling in the MFA samples. - Appl. Phys. Lett.105, 072905 (2014); J. Appl. Phys. 117, 17B904 (2015)

(c) Magneto-dielectric effect in core-shell particles: Magneto-dielectric effects (MDE) in self-assembled core-shell nanoparticles of NFO/BTO were investigated in the millimeter wave frequencies. The core-shell composites were synthesized by coating 100 nm NFO and 50 nm BTO with complementary coupling groups and allowing them to self-assemble in the presence of a catalyst forming heterogeneous nanocomposites. ME characterization of as-assembled particles were carried out by measurements of the relative permittivity as a function of frequency f under an applied static magnetic field H over 16-24 GHz. Measurements show an H-induced decrease of 1 to 1.5% in the permittivity. But a giant magneto-dielectric effect with an H-induced change in permittivity as high as 28% was measured under dielectric resonance in the samples. A theory for the high frequency magneto-dielectric effect was developed and theoretical estimates were in general agreement with the data. - AIP Advances 4, 097117 (2014); J. Appl. Phys. 117, 17A309 (2015)

2. DNA-assisted assembly of core-shell particles and studies on ME interactions
(a) Nanoparticle Assembly with DNA/RNA: The approach involves covalently attaching organic functional groups or oligomeric DNA/RNA to the nanoparticles. The organic functional groups are only reactive towards functional groups located on different nanoparticles. Using oligomeric DNA/RNA, one could program nanoparticles to only interact with particles possessing complementary DNA/RNA. We have applied both concepts to the assembly of nanostructures with ferrites for the ferromagnetic phase and barium titanate for the ferroelectric phase. DNA-assisted self-assembly involved oligomeric DNA-functionalized NFO and BTO. Mixing the particles, possessing complementary DNA sequences, resulted in the formation of ordered core-shell heteronanocomposites held together by DNA hybridization. The composites were imaged by scanning electron microscopy and scanning microwave microscopy. - AIP Advances_6, 045202 (2016), MRS Commun 20, 7 (2017)

(b) Magnetic field assembly of superstructures: The reversible nature of the DNA hybridization allows for restructuring the composites into mm-long linear chains and 2D-arrays in the presence of a static magnetic field and ring-like structures in a rotating-magnetic field. Strong ME coupling in as-assembled composites was evident from static magnetic field H induced polarization and low-frequency magnetoelectric voltage coefficient measurements. Upon annealing the nanocomposites at high temperatures, evidence for the formation of bulk composites with excellent cross-coupling between the electric and magnetic subsystems was obtained by H-induced polarization and low-frequency ME voltage coefficient. - AIP Advances_6, 045202 (2016)

(c) Studies on dependence of ME interactions on nature of DNA-base pairs: Ferrite-ferroelectric core-shell nanoparticles were prepared by DNA assisted assembly. The nanoparticle size were varied and the DNA linker sequence was also varied by using DNA containing 19, 18 or 30 base pairs. Films and disks of the core-shell particles were assembled in a magnetic field and used for measurements of low frequency MEVC and magnet-dielectric effect. The MEVC data on films indicate that particles assembled with DNA with 30 base pairs exhibit the strongest ME coupling suggesting a more fully integrated heterogenous nanocomposite and the weakest interaction for DNA with 18 base pairs. These results indicate that the longer linker region in DNA is the key factor for forming better composites. Shorter strands would not able to bridge the irregularly shaped particles as well and therefore result in linkages and less heterogeneity in the composites. - Journal of Magnetism and Magnetic Materials 460, 424 (2018)

3. Coaxial nanofibers of ferrites and ferroelectrics

(a) Nickel ferrite-PZT core-shell fibers: Core-shell nanofibers of nickel ferrite and lead zirconate titanate were synthesized by electrospinning, assembled into superstructure in uniform or non-uniform magnetic fields, and have been characterized in terms of ferroic order parameters and ME coupling. The core-shell structure was confirmed by electron microscopy and scanning probe microscopy. Studies on magnetic field induced polarization P in assembled samples showed a decrease or increase in P, depending on the nature of fibers, and strengthening of ME coupling with change in remnant-P as high as 32%. Strong ME interactions were also evident from H-induced variation in permittivity at 20-22 GHz. - Appl. Phys. Lett. 104, 052910 (2014)

(b) Ferrite-Barium titanate core-shell nanowires: We reported synthesis of NFO-BTO core-shell nano-fibers, magnetic field assisted assembly into superstructures, and studies on ME interactions. Electrospinning techniques were used to prepare coaxial fibers of 0.5-1.5 micron in diameter. The fibers were assembled into discs and films in a uniform magnetic field or a field gradient. Studies on ME coupling in the assembled films showed ~ 2-7% change in remnant polarization and in the permittivity for H = 7 kOe and a MEVC of 0.4 mV/cm Oe at 30 Hz. A model was developed for low-frequency ME effects in an assembly of fibers and takes into account dipole-dipole interactions between the fibers and fiber discontinuity. Theoretical estimates for the low-frequency MEVC have been compared with the data.- Materials 2018, 11, 18

Training Opportunities: The support facilitated research training for:

- 3 Postdoctoral Research Associates

- 3 Graduate Students

- 5 Undergraduates (3 supported by ARO-URAP grants)

- 2 High school students.

The postdocs and students were involved in the synthesis of nanocomposites and structural, magnetic, ferroelectric and magneto-electric characterization of the composites.

Results Dissemination: Results were published in 18 peer reviewed journal articles and 15 invited and contributed presentations in conferences.

Honors and Awards: AWARDS
Two high school students, Mr. Aditya Mukundan (sophomore/junior, International Academy, Troy, MI) and Ms. Neha Bidthanapally (sophomore/junior, Rochester High School) participated in the ARO-supported research during 2013-14. They won the following awards.

1. Aditya Mukundan

Project Title: Magnetic and Piezoelectric Core-Shell Nanofibers for Applications in Medicine

Competition: 54th Intel – Science and Engineering Fair of Metro Detroit and 19th Annual Michigan Science Fair. March and April, 2013 (at Detroit and at Kettering University, Flint, Michigan).

Awards: Pewter Medallion by Yale Science & Engineering Association, Inc.
$1000 by the Society of Oncologist

2. Aditya Mukundan and Neha Bidthhanapally
Project Title: Novel core-shell multiferroic fibers with potential for use in biomagnetic imaging
Competition: Siemens Competition: Math: Science: Technology
Award: Regional Semifinalists (made oral and poster presentations at the University of Notre Dame), Nov. 2013.
$1000 scholarship for each student. Their schools were awarded $1000 each.

3. Aditya Mukundan
Project Title: Self-Assembled Nanometer Sized Magnetic Sensors and Arrays for Biomagnetic imaging
Competition: 2015 INTEL Science Talent Search
Award: Semifinalist.
$1000 each scholarship. Their schools were awarded $1000 each.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: Gopalan Srinivasan
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Co-Investigator
Participant: Ferman Chavez
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Vladimir Petrov
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:

International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Gollapudi Sreenivasulu
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Maksym Popov
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Rue Zhang
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Clavis Janes
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Kharananda Sharma
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Manashi Panda
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:

International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Amit Diwakar
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Samip Gandhi
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Crystal Benoit
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Sean Hamilton
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Undergraduate Student
Participant: Piper Lehto
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: High School Student
Participant: Aditya Mukundan
Person Months Worked: 6.00 **Funding Support:**

Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: High School Student
Participant: Neha Bidthanapally
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

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Volume: 0 Issue: 0 First Page #: 0
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Publication Location:
Article Title: Magnetoelectric coupling in solution derived 3-0 typePbZr0.52Ti0.48O3:xCoFe2O4 nanocomposite films
Authors:
Keywords: Magnetoelectric, composite
Abstract: Magnetoelectric (ME) coupling (aE) in piezoelectric:magnetostrictive composites is mediated through mechanical strain at their interfaces. Incorporating magnetic nanoparticles (NPs) in piezoelectric matrix enhances interfacial area between the two phases and therefore large aE can be expected. Here, we present electric and ME properties of 3-0 type nanocomposite thin films with various concentrations of $CoFe_2O_4$ NPs dispersed in $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) matrix. Nanocomposite films show only a slight reduction in remnant electric-polarization as compared to that of PZT. A nanocomposite film with 0.1% $CoFe_2O_4$ (molar concentration) exhibited the highest transverse aE of 549 mV/cmOe at 453 Oe dc bias and 1 kHz
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Publication Type: Journal Article Peer Reviewed: N **Publication Status:** 1-Published
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Publication Identifier Type: Publication Identifier:
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: ZnO/LSMO Nanocomposites for Energy Harvesting
Authors:
Keywords: nanocomposite, multiferroic
Abstract: The composites of strontium-doped lanthanum manganite (LSMO) with zinc oxide (ZnO) are candidate materials for energy harvesting by virtue of their magnetic and piezoelectric characteristics. They could be used to harvest energy from stray sources, such as the vibrations and electromagnetic noise from transformers and compressors within electrical grid power stations to power small diagnostic sensors, among other applications. The LSMO/ZnO nanocomposites were made by: (i) milling the two bulk powders and, (ii) a wet chemical process which resulted in core-shell structures. The electrical, piezoelectric, and magnetoelectric properties showed strong dependence on the fabrication method. Growth of ZnO nanopillars on the particulate core of LSMO surface appears to have improved the piezoelectric properties. Moreover, the chemical bath deposition process can be easily modified to incorporate dopants to augment these properties further.
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Journal: Appl. Phys. Lett.
Publication Identifier Type: Publication Identifier:
Volume: 0 Issue: 0 First Page #: 0
Date Submitted: Date Published:
Publication Location:
Article Title: Controlled Self-assembly of Multiferroic Core-Shell Nanoparticles Exhibiting Strong Magneto-electric Effects
Authors:
Keywords: Self-assembly, ferrite, ferroelectric, multiferroic
Abstract: Ferromagnetic-ferroelectric composites show strain mediated coupling between the magnetic and electric sub-systems due to magnetostriction and piezoelectric effects associated with the ferroic phases. We have synthesized core-shell multiferroic nano-composites by functionalizing 10-100 nm barium titanate and nickel ferrite nanoparticles with complementary coupling groups and allowing them to self-assemble in the presence of a catalyst. The core-shell structure was confirmed by electron microscopy and magnetic force microscopy. Evidence for strong strain mediated magneto-electric coupling was obtained by static magnetic field induced variations in the permittivity over 16-18 GHz and polarization and by electric field induced by low-frequency ac magnetic fields.
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Volume: 0 Issue: 0 First Page #: 0
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Article Title: Magnetic Field Assisted Self-assembly of Ferrite-Ferroelectric Core-Shell Nanofibers and Studies on Magneto-electric Interactions
Authors:
Keywords: Magnetic field directed assembly, core-shell fibers, ferrite, ferroelectric
Abstract: Core-shell nanofibers of nickel ferrite and lead zirconate titanate have been synthesized by electrospinning, assembled into superstructure in uniform or non-uniform magnetic fields, and have been characterized in terms of ferroic order parameters and strain mediated magneto-electric (ME) coupling. The core-shell structure was confirmed by electron microscopy and scanning probe microscopy. Studies on magnetic field induced polarization P in assembled samples showed a decrease or increase in P, depending on the nature of fibers, and strengthening of ME coupling with change in remnant-P as high as 32%. Strong ME interactions were evident from H-induced variation in permittivity at 20-22 GHz.
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Authors:
Keywords: ferrite, ferroelectric, microwave, millimeter wave
Abstract: There have been considerable interests in recent years in ferrite-ferroelectric composites for dual magnetic- and electric field tunable microwave and mm-wave devices such as resonators, filters, and phase shifters. Low-loss spinel and hexagonal ferrites are used in high frequency devices and the tuning in general is with a magnetic field H. When the ferrite is replaced by a ferrite-ferroelectric composite, however, the piezoelectric strain due to an electric field E applied to the ferroelectric will manifest as an induced anisotropy in the ferrite and facilitate E-tuning of the device. This review focuses on recent efforts on voltage tunable ferrite filters. A related phenomenon of importance is the nature of magneto-dielectric resonance in ferrites and its potential for low-loss H-tunable dielectric resonators, filters, isolators, and phase shifters for the frequency range 18-110 GHz. Potential avenues for enhancing the E-tuning of ferrite devices are also addressed.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

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Publication Identifier Type: DOI Publication Identifier: 10.1179/1743284714Y.0000000537
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Date Submitted: Date Published:
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Article Title: Multiferroic oxide composites: synthesis, characterisation and applications

Authors:

Keywords: Mulriferroic composite, ferrite, ferroelectric

Abstract: The nature of mechanical strain mediated electromagnetic coupling in multiferroic composites has been studied extensively in recent years. This review is on composites with ferromagnetic or ferrimagnetic oxides and ferroelectrics. Systems studied so far include samples with spinel ferrites, hexagonal ferrites or lanthanum manganites for the ferromagnetic phase and barium titanate, PZT, PMN-PT, or PZN-PT for the ferroelectric phase. Bilayer and multilayer heterostructures, bulk composites, core-shell nanoparticles, and core-shell nanotubes and nanowires were investigated for their response to magnetic fields, termed direct magnetoelectric effect (DME). Several systems show a giant low-frequency DME and resonance enhancement at bending and electromechanical resonance. The response of the composites to an electric field, called converse ME effect, is found to be strong in several ferrite-ferroelectric composites. The potential for use of the composites for pico-Tesla magnetic senso

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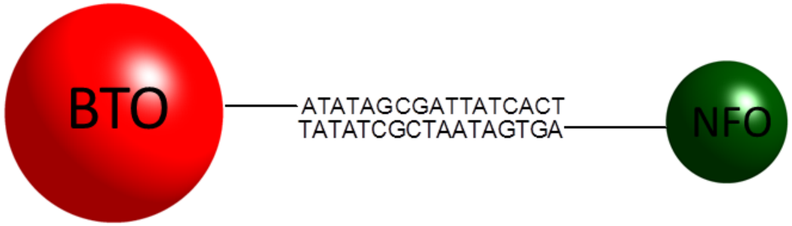
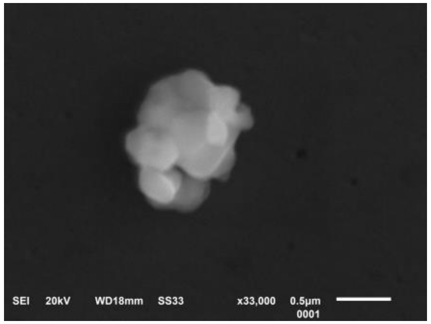
Self-Assembled Multiferroic Nanostructures and Studies on Magneto-electric Interactions (W911NF 121 0545)

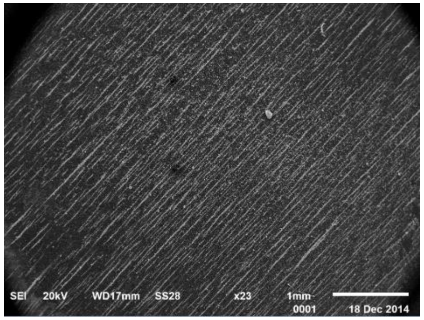
Final report

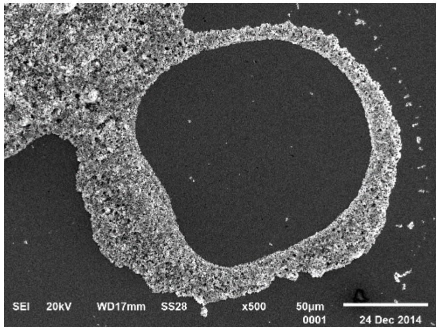
Scientific accomplishments

Gopalan Srinivasan (PI), Oakland University, Rochester, MI









2. Table of Contents

Publications

1. “ZnO/LSMO nanocomposites for energy harvesting,” R. Kinner, A. Azad, G. Srinivasan, G. Sreenivasulu, and M. Jain, Smart Nano. Sys. Eng. Med. 2, (2012).
2. “Magnetoelectric coupling in solution derived 3-0 type $PbZr_{0.52}Ti_{0.48}O_3$: $CoFe_2O_4$ nanocomposite films,” A. McDannald, M. Staruch, G. Sreenivasulu, C. Cantoni, G. Srinivasan, and M. Jain, Appl. Phys. Lett. 102, 122905 (2013).
3. Gollapudi Sreenivasulu, Maksym Popov, Ferman A. Chavez, Sean L. Hamilton,Piper R. Lehto, and Gopalan Srinivasan, “Controlled Self-assembly of Multiferroic Core-Shell Nanoparticles Exhibiting Strong Magneto-electric Effects, “ Appl. Phys. Lett. 104, 052901 (2014).
4. G. Sreenivasulu, Maksym Popov, Ru Zhang, K. Sharma, C. Janes, A. Mukundan, and G. Srinivasan, “Magnetic Field Assisted Self-assembly of Ferrite-Ferroelectric Core-Shell Nanofibers and Studies on Magneto-electric Interactions,” Appl. Phys. Lett. 104, 052910 (2014).
5. G. Srinivasan, I. V. Zavislyak, M. Popov, G. Sreenivasulu, and Y. K. Fetisov, “Ferrite-Piezoelectric Heterostructures for Microwave and Millimeter Devices: Recent Advances and Future Possibilities,” J. Jpn. Soc. Powder and Powder Metallurgy, 61, S25 (2014).
6. G. Sreenivasulu, H. Qu, and G. Srinivasan, “Multiferroic oxide composites: synthesis, characterization and applications,” Mater. Sci. Tech. 2014. (DOI 10.1179/1743284714Y.0000000537.)
7. “Magneto-electric Effects in Functionally Stepped Magnetic Nanobilayers on Ferroelectric Substrates: Observation and Theory on the Influence of Interlayer Exchange Coupling,“ I.V.Gribov, V.I.Osotov, A.P.Nosov, V. M. Petrov, G. Sreenivasulu, and G. Srinivasan, J. Appl. Phys. 115, 193909 (2014).
8. “Superstructures of self-assembled multiferroic core-shell nanoparticles and studies on magneto-electric interactions,” G. Sreenivasulu, V. M. Petrov, F. A. Chavez, and G. Srinivasan, Applied Physics Letters 105, 072905 (2014).
9. “Magnetic Field Directed Assembly of Superstructures of Ferrite-Ferroelectric Core-Shell Nanoparticles and Studies on Magneto-electric Interactions,” G. Srinivasan, G. Sreenivasulu, Crystal Benoit, V. M. Petrov, and F. Chavez, J. Appl. Phys. 117, 17B904 (2015).
10. “Millimeter-wave Magneto-Dielectric Effects in Self-assembled Ferrite-Ferroelectric Core-Shell Nanoparticles,” G. Srinivasan, M. Popov, G. Sreenivasulu, V. M. Petrov, and F. Chavez, J. Appl. Phys. 117, 17A309 (2015).

11. “Self-Assembly of Multiferroic Core-Shell Particulate Nanocomposites through DNA-DNA Hybridization and Magnetic Field Directed Assembly of Superstructures,” Gollapudi Sreenivasulu, Thomas A. Lochbiler, Manashi Panda, Gopalan Srinivasan, and Ferman A. Chavez, AIP Advances 6, 045202 (2016).

12. “The 2016 Oxide Electronic Materials and Oxide Interfaces Roadmap,” M. Lorenz, M. S. Ramachandra Rao, T Venkatesan, E. Fortunato, P. Barquinha, R. Branquinho, D. Salgueiro, R. Martins, E. Carlos, A. Liu, F. K. Shan, M. Grundmann, H Boschker, J. Mukherjee, M. Priyadarshini, N. DasGupta, D. J. Rogers, F. H. Tehrani, E. V. Sandana, P. Bove, K. Rietwyk, A. Zaban, A. Veziridis, A. Weidenkaff, M.Muralidhar, M. Murakami, S. Abel, J. Fompeyrine, J. Zuniga-Perez, R. Ramesh, N. Spaldin, S. Ostanin, VBorisov, I. Mertig, V. Lazenka, G.Srinivasan, W. Prellier, M. Uchida, M. Kawasaki, R. Pentcheva, P.Gegenwart, F. Miletto, Granozio, J. Fontcuberta, N. Pryds, J. Phys.D: Appl. Phys. 49, 433001 (2016).

13. F. A. Chavez and G. Srinivasan, Self assembly of nanostructures with multiferroic components using nucleic acid linkers, MRS Commun. 7, 20 (2017).

14. McDannald, Austin, Linghan Ye, Claudia Cantoni, Sreenivasulu Gollapudi, Gopalan Srinivasan, Bryan D. Huey, and Menka Jain. "Switchable 3-0 magnetoelectric nanocomposite thin film with high coupling." *Nanoscale* 9, no. 9 (2017): 3246-3251.

15. Vopson, M. M., Y. K. Fetisov, G. Caruntu, and G. Srinivasan. "Measurement techniques of the magneto-electric coupling in multiferroics." *Materials* 10, no. 8 (2017): 963.

16. Petrov, Vladimir, Jitao Zhang, Hongwei Qu, Peng Zhou, Tianjin Zhang, and Gopalan Srinivasan. "Theory of Magnetoelectric Effects in Multiferroic Core-Shell Nanofibers of Hexagonal Ferrites and Ferroelectrics." *Journal of Physics D: Applied Physics* (2018).

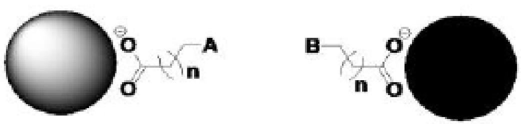
17. Viehland, Dwight, Jie Fang Li, Yaodong Yang, Tommaso Costanzo, Amin Yourdkhani, Gabriel Caruntu, Peng Zhou, Tianjin Zhang, Tianqian Li, Arunava Gupta, Maksym Popov, Gopalan Srinivasan. "Tutorial: Product properties in multiferroic nanocomposites." *Journal of Applied Physics* 124, no. 6 (2018): 061101.

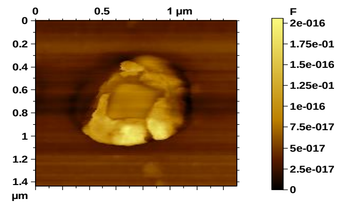
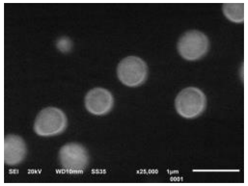
18. Banerjee, Atanu, Jitao Zhang, Peng Zhou, Koushik Tuppil, Gollapudi Sreenivasulu, Hongwei Qu, Tianjin Zhang, Roshan Timilsina, Ferman A. Chavez, and Gopalan Srinivasan. "Self-assembly of multiferroic core-shell composites using DNA functionalized nanoparticles." *Journal of Magnetism and Magnetic Materials* 460 (2018): 424-431.

Major Tasks Completed

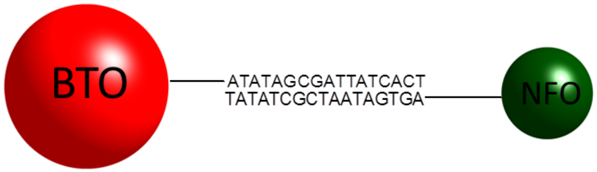
Strain mediated magneto-electric coupling in magnetostrictive-piezoelectric nanocomposites:

1. Core-shell Nanoparticles - Chemical self-assembly

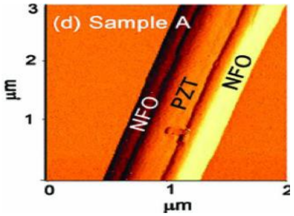


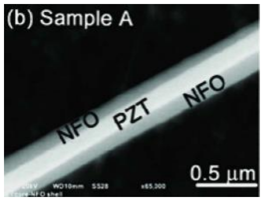



- Functionalized-DNA assisted assembly



2. Core-shell Nanowires





I. Core-shell Particles: Chemical Self-Assembly

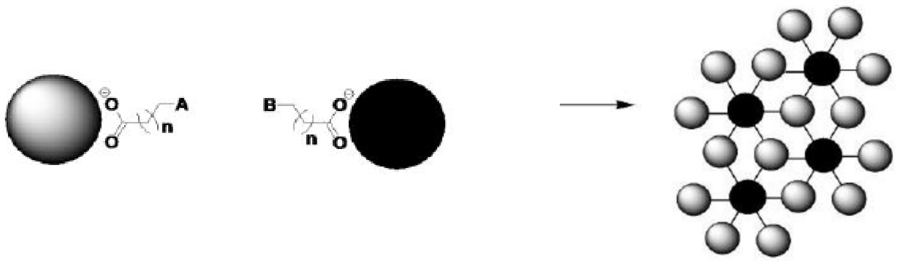
Chemical self-assembly of core-shell barium titanate (BTO) and nickel ferrite, Ni Fe_2O_4 (NFO) particles

SEM, TEM, MFM, SMM

Magnetic and ferroelectric characterization

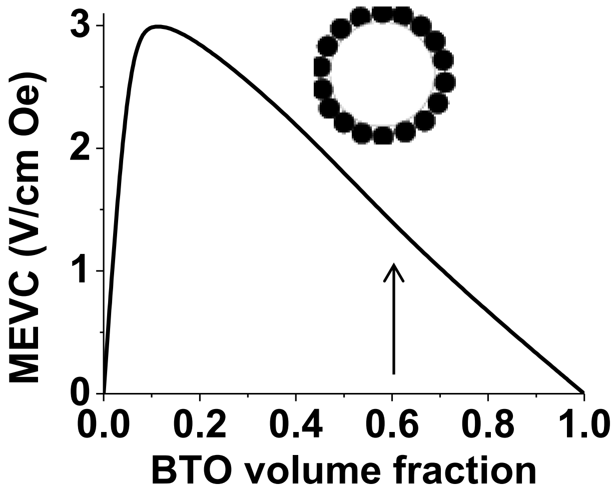
Assembly of superstructures in uniform/nonuniform magnetic field

Magneto-electric coupling
- P vs E under H
- Magneto-dielectric effect
- ME voltage coefficients (1 mHz – 1 kHz)



Theory

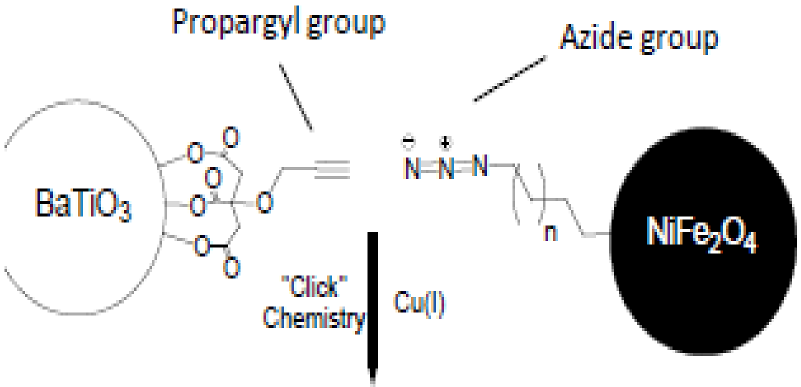
50 nm $BaTiO_3$ core
10 nm $NiFe_2O_4$shell



<u>Motivation:</u>
Ideal for synthesizing bulk composites with:
desired connectivity and control over volume ratio.

<u>What is predicted by theory?</u>
- an order of magnitude stronger ME coupling than in traditional sintered composites.

“Click-reaction” aided assembly of core-shell ferrite-ferroelectric nanoparticles



Procedure:

Step 1: Synthesis of $BaTiO_3$ (BTO) and $NiFe_2O_4$ (NFO) nanoparticles by coprecipitation

Step 2: Functionalize with complementary coupling groups (Alkyn and Azide groups)

Step 3: Allow copper catalized self-assembly:

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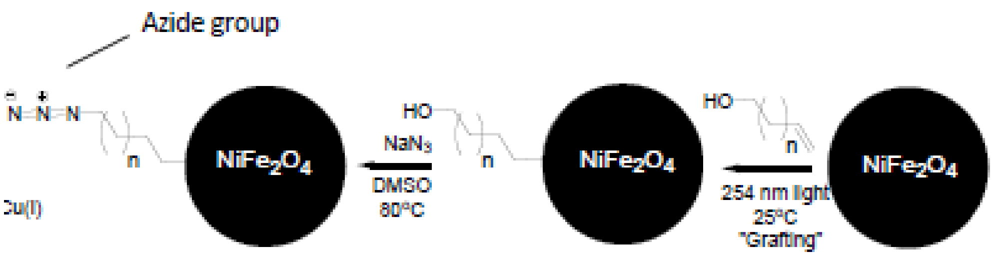
Functionalizing with azide group: NFO (or BTO)



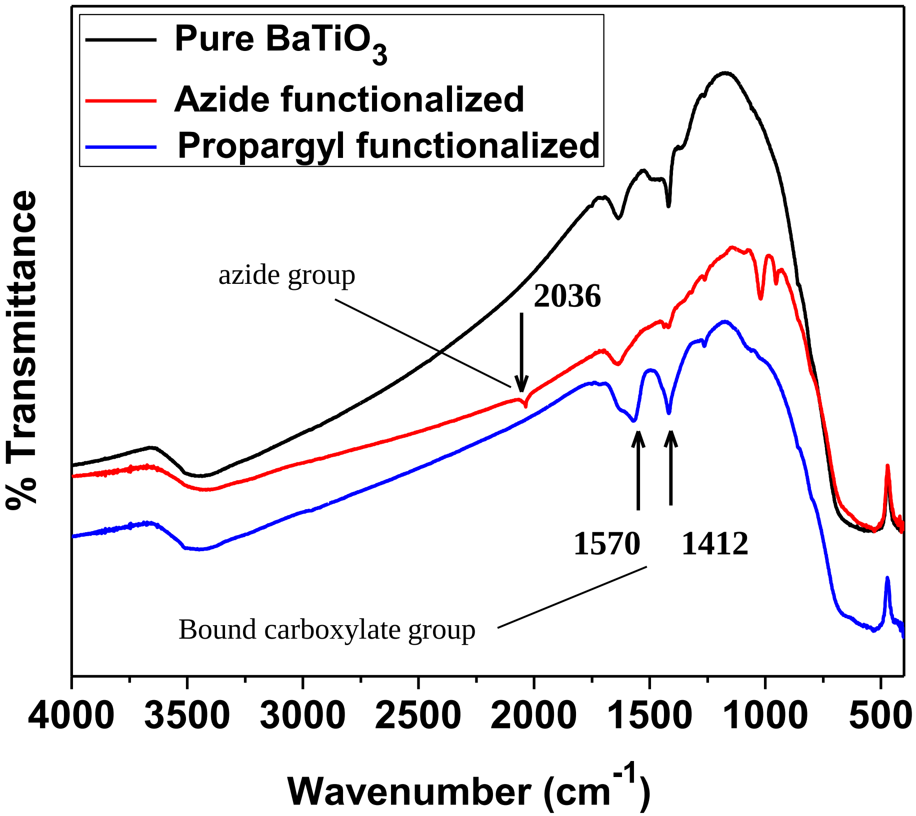
1. NFO (or BTO) was coated with 3-buton-1-ol, sealed in Ar-purged cell and exposed to UV (254 nm; 15 mW/cm^2)

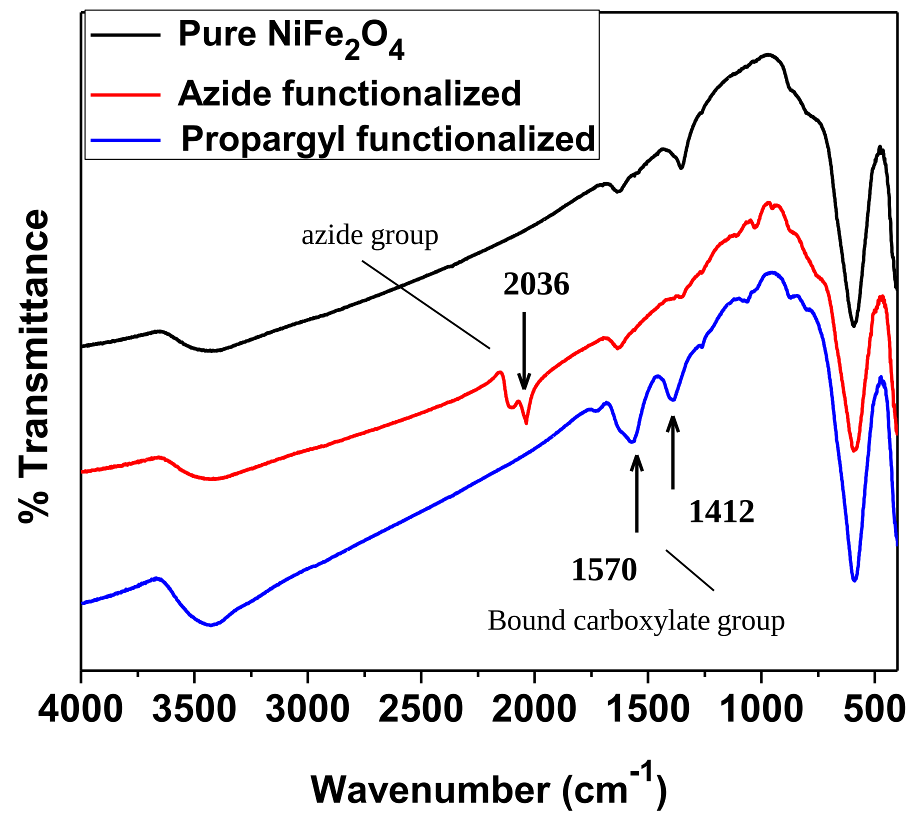
2. Rinsed with methanol, $CHCl_3$, IPA. Then OH group was converted to methanesylfonyl (mesyl) group by further chemical processing.

3. Mesyl group was converted to azide group by immersing the particles in NaN_3 and dimethlysulfide (DSMO)

Functionalizing with alkyn group: NFO (or BTO)

With o'propargyl citric acid

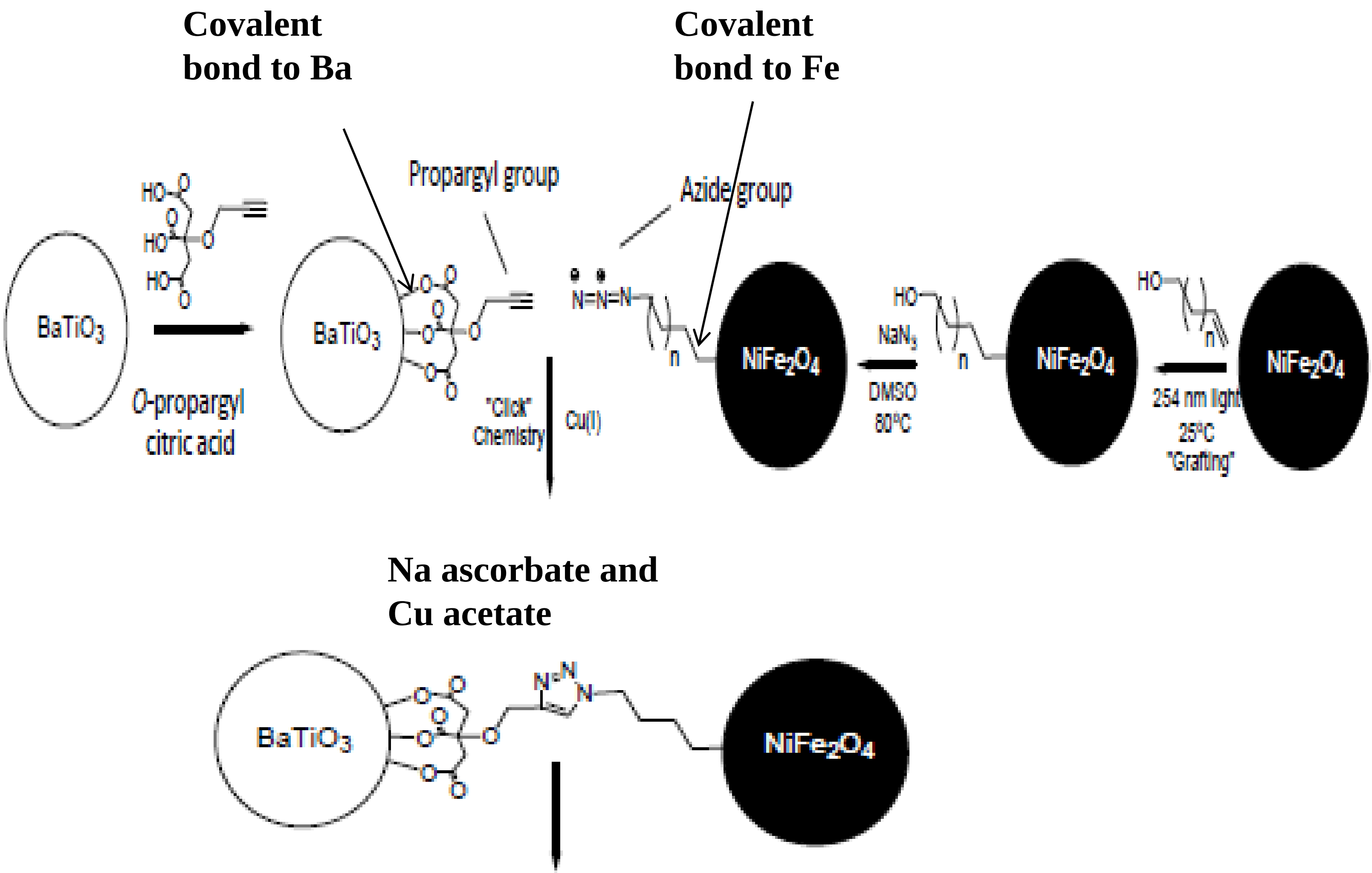




Attachment verified by IR spectroscopy

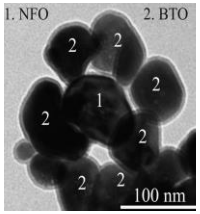
BTO and NFO successfully functionalized by both groups.

IR Spectra of $BaTiO_3$ and $NiFe_2O_4$ show attachment of Azide OR alkyn (Propargyl) group.


Covalent bond to Ba
Covalent bond to Fe
Propargyl group
Azide group
BaTiO3
O-propargyl citric acid
"Click" Chemistry
Cu(I)
NiFe2O4
NaN3
DMSO
80°C
254 nm light
25°C
"Grafting"
Na ascorbate and Cu acetate

Systems studied:
50-600 nm barium titanate (BTO) and 10-400 nm ferrite

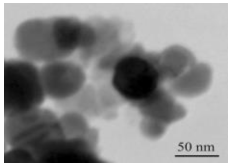
100 nm NFO; 50 nm BTO



8 - BTO around the core in 2D
16 – BTO around the core in 3D

Sample A

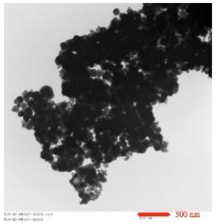
50 nm BTO; 10 nm NFO



19 NFO around the core in 2D
78 NFO around the core 3D

Sample B

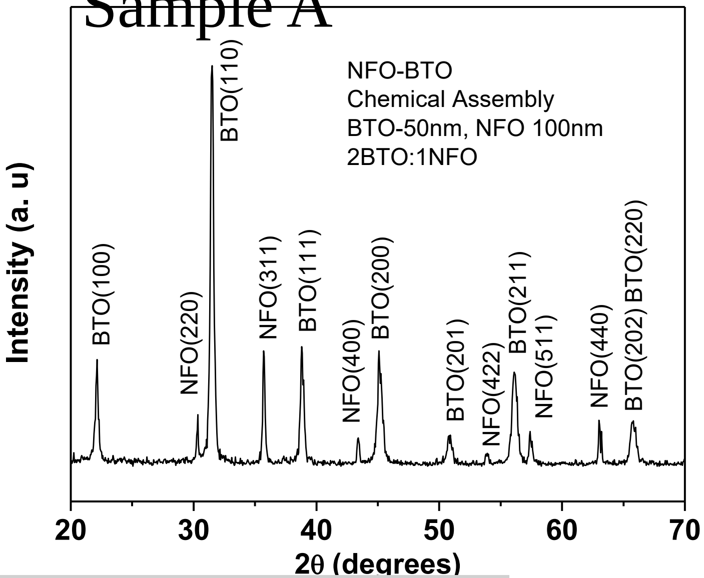
100 nm BTO; 10 nm NFO



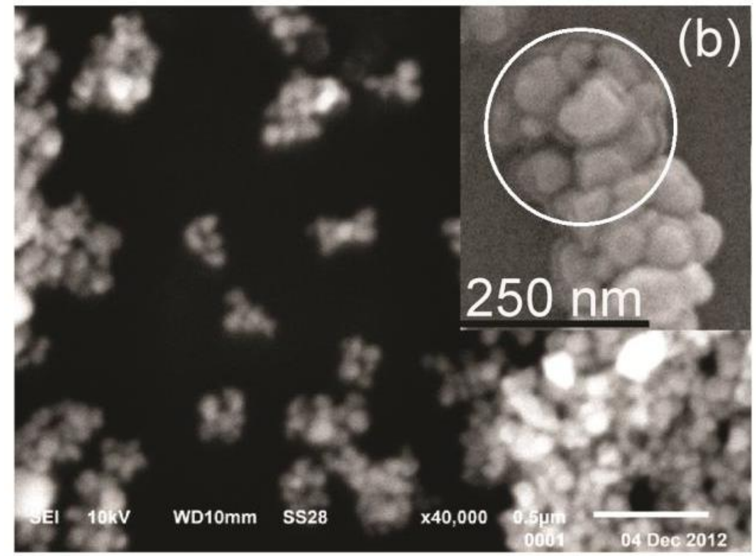
Sample C

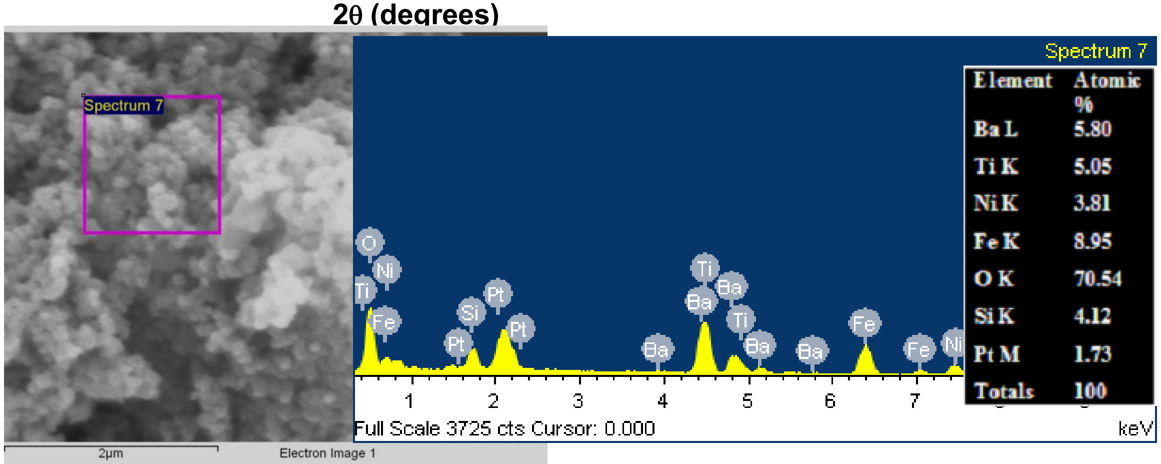
Structural Characterization: SEM, TEM, MFM, SMM, XRD

50 nm BTO; 100 nm NFO – Sample A



SEM





-Clusters evident from SEM

-Absence of impurity phases

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600 nm BTO core – 200 nm Ni ferrite shell

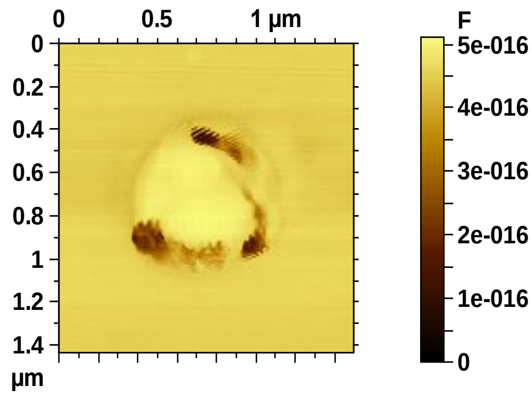
Capacitance images at frequencies 2-20 GHz

Scanning microwave microscopy of core-shell particles

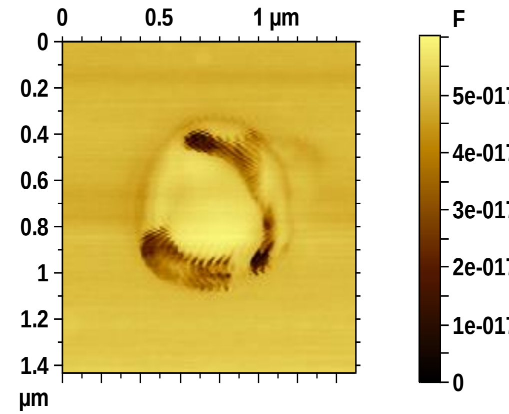
Agilent Scanning Microwave Microscope (SMM).

Iimpedance and capacitance mapping at 1 to 26 GHz

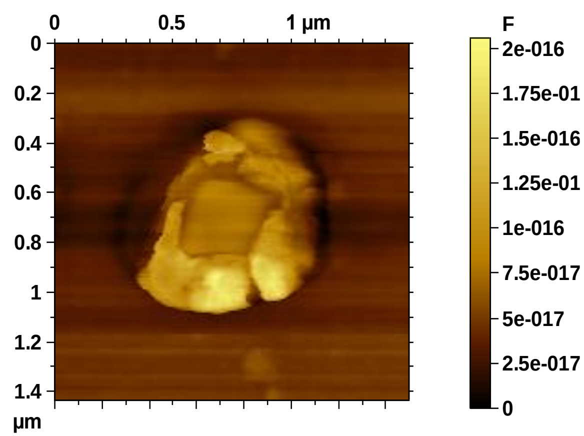
The SMM capacitance (permittivity) images at 2-20 GHz show the core-shell structure for 600 nm BTO/ 200 nm NFO.



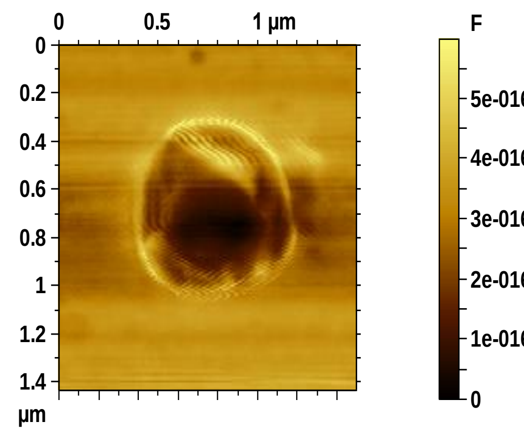
2.3 GHz



7.3 GHz

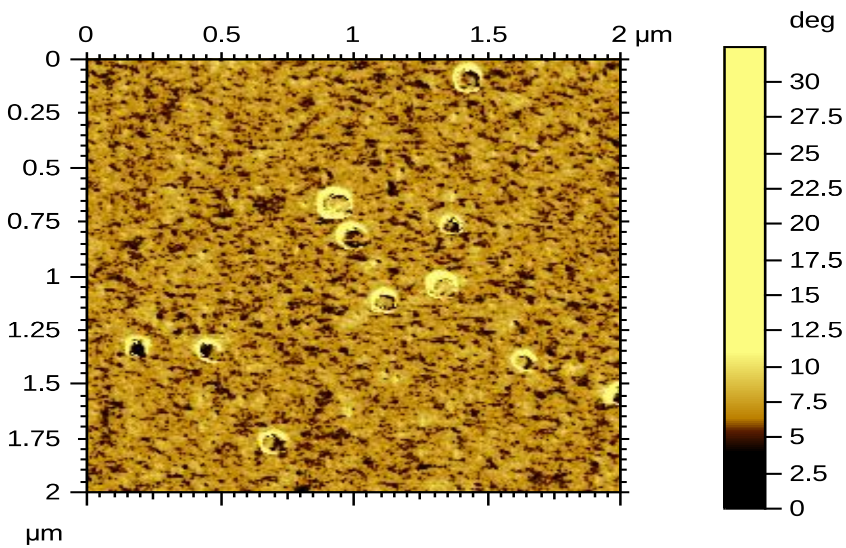


14 GHz



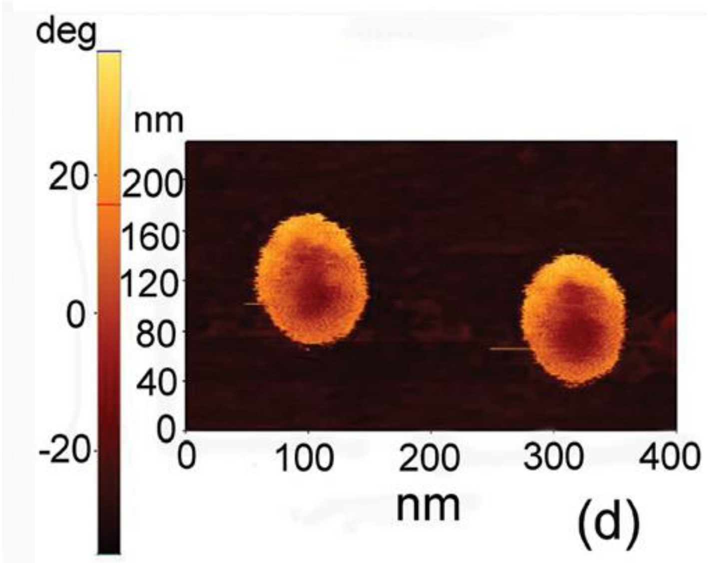
19 GHz

SMM phase image at 16 GHz



SMM-Phase for collection of particles of sample-A

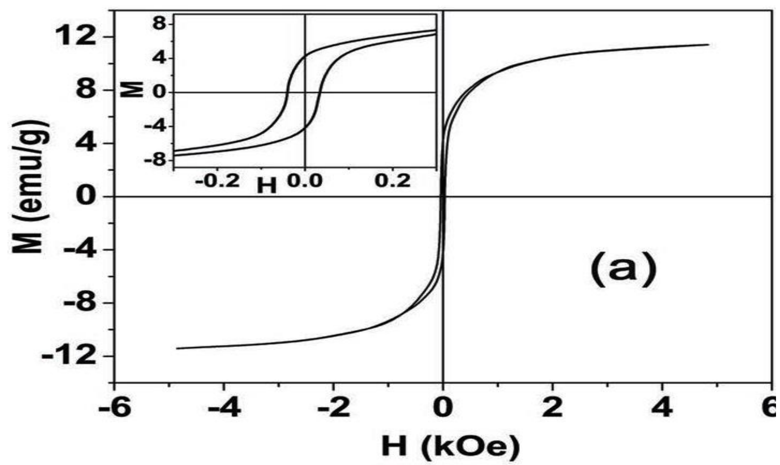
MFM for core-shell



MFM-Phase for collection of core-shell particles of sample-B

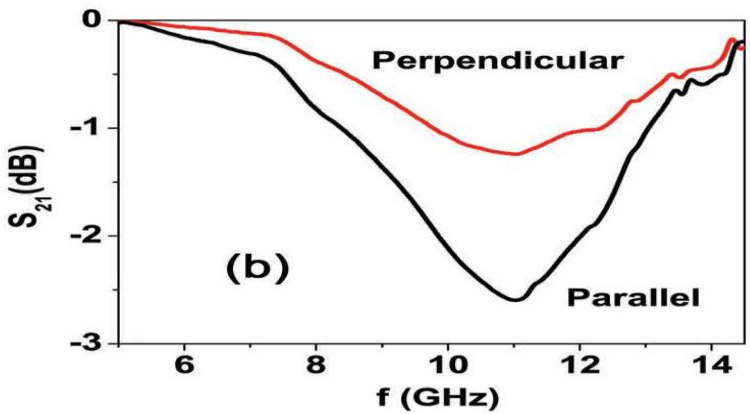
Magnetic characterization

Magnetization



Composites are ferromagnetic with M expected for bulk ferrites

FMR for sample-A

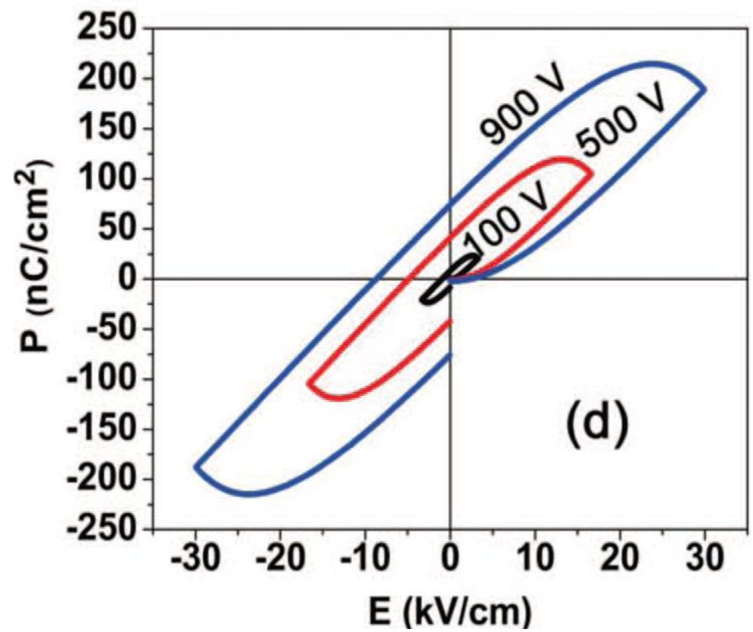


Ferromagnetic resonance (FMR) derived magnetic parameters in agreement with bulk-like magnetic parameters for ferrite in the particles.

Ferroelectric characterization

P vs E show ferroelectric behavior for the ferrite-BTO particles (sample-C).

Remnant polarization and coercivity are smaller than for thin film BTO.



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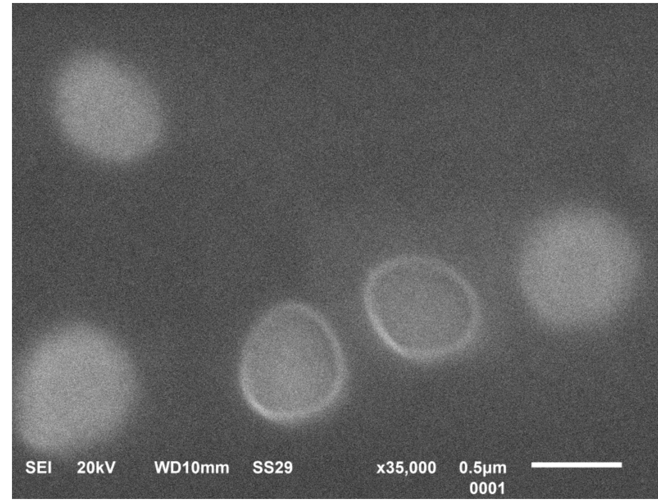
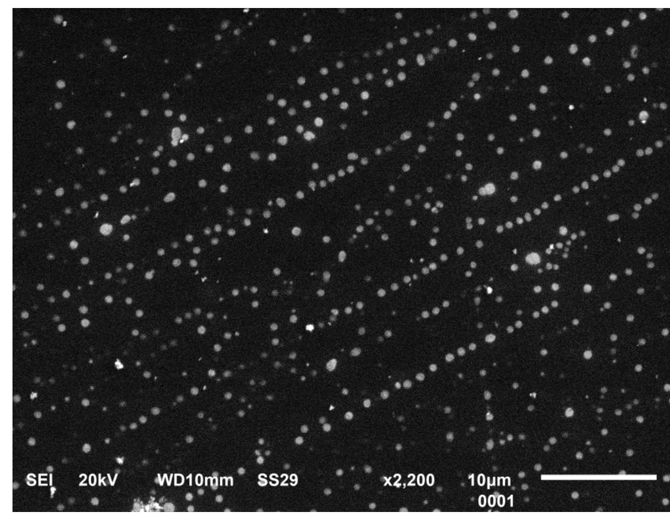
Magnetic Field Assisted Assembly (MFAA) of Superstructures of Core-Shell ferrite/BTO Particles

Core-shell particles were further assembled into 1D and 2D superstructures in:



(i) <u>a uniform magnetic field</u> that is expected to assemble the particles into parallel chains.

(i) <u>a nonuniform field</u> created by a permanent magnet that exerts an attractive force on the particles and align them toward the regions of high field strengths.



100 nm BTO-10nm NFO core-shell particles: Assembly into 1D chain in a uniform field

SEM micrographs of 1D chains obtained in a uniform field generated by an electromagnet

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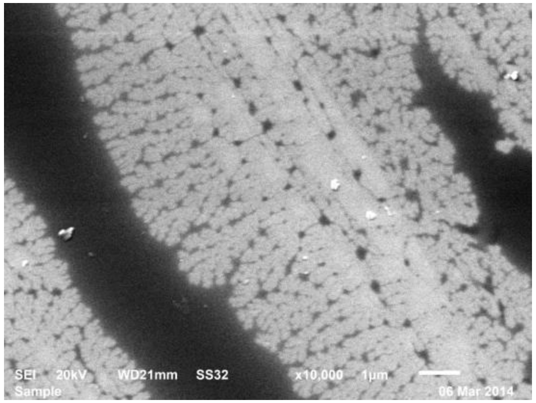
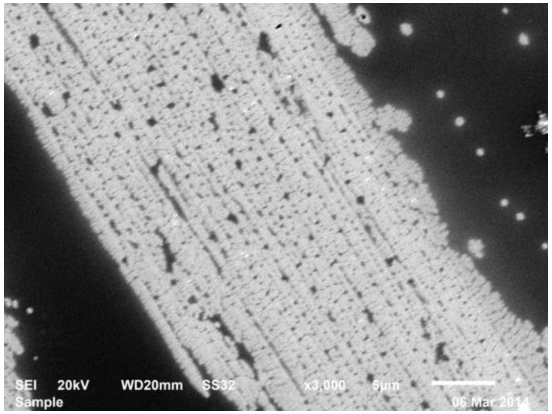
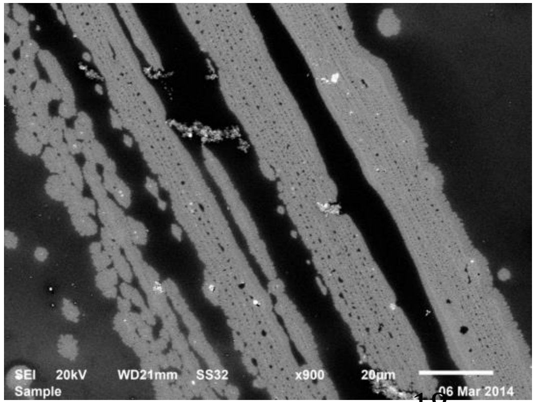
Assembly in a non-uniform field







100 nm BTO-10nm NCFO core-shell particles assembled into a 2D film in a magnetic field created by a permanent magnet.

Regions of high particle concentration correspond to high magnetic field strengths.

A fine structure is seen at the edges of these regions and is due to nonuniform magnetic field created by the particles at the edge that promote the growth of perpendicular chains.

Low-frequency Magneto-electric effects in H-assembled 2D/3D structures

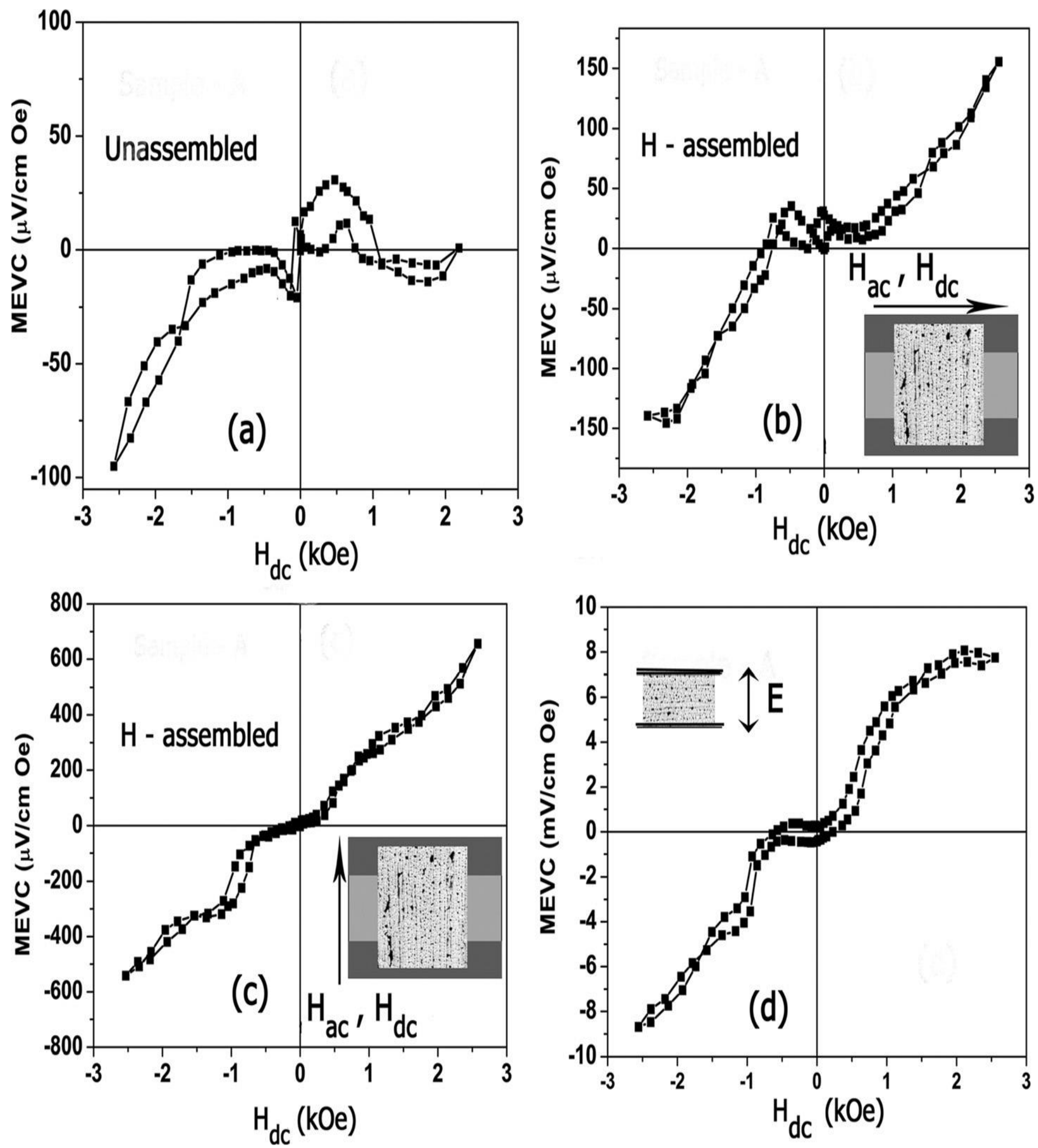
Low-frequency ME measurements were done on films assembled between two electrodes on a glass slide.

The ME voltage coefficient was measured by applying a DC bias magnetic field and AC field parallel to the electrodes.

Data on MEVC vs H are shown for Sample with 100 nm NFO core and 50 nm BTO shell.

The strongest ME effect is measured in MFAA-films.

Maximum MEVC ~ 8 mV/cm Oe



Appl. Phys. Lett 105, 072905 (2014)

First-principles theory of low-frequency ME effect in H-assembled linear chains and 2D arrays

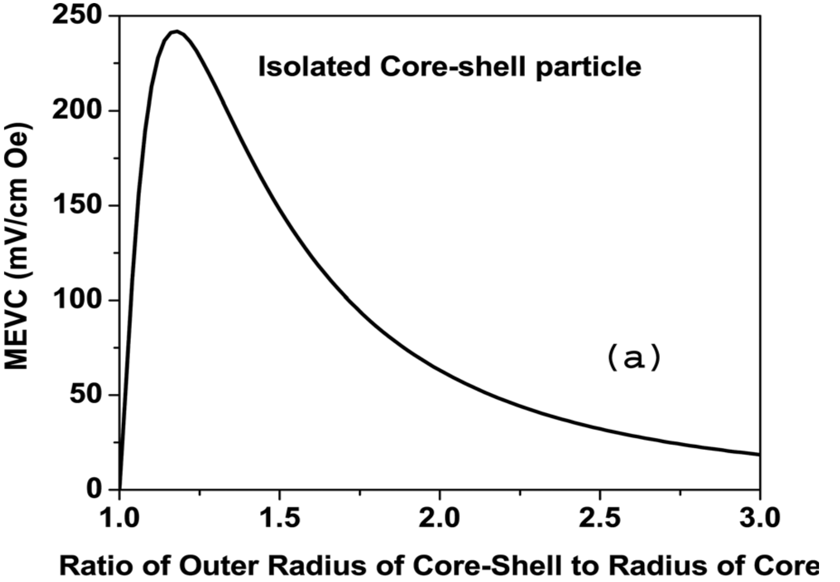
From free-energy considerations the ME voltage coefficient for an isolated core-shell particle is estimated as a function of ratio of the outer radius of the core-shell to radius of the core and shown in the figure (a).

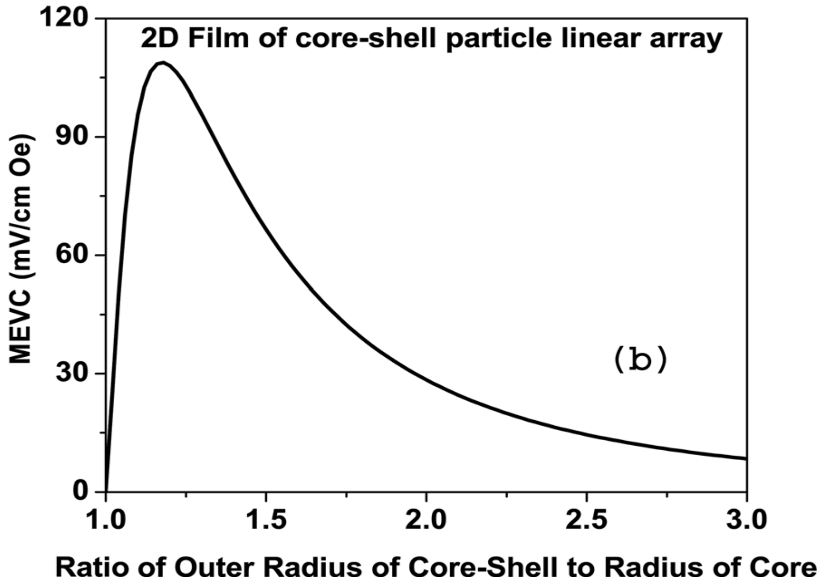
The theory predicts MEVC as high as 240 mV/cm Oe for isolated particles.

The model is then extended to a film made of parallel linear arrays of particles of uniform diameter.

For simplicity each chain is assumed to contain n=10 nanoparticles.

The overall ME coupling shown in the figure (b) is weaker in the film made up of the arrays than for an isolated particle and is due to the dipole-dipole interactions that lead to a reduction in the net magnetization and polarization and weakening of the magnetostriction and piezoelectric effects.





Magneto-dielectric effect (MDE): 16-42 GHz

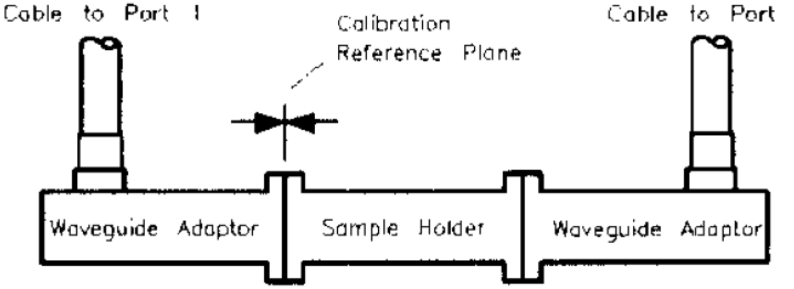
-Agilent Vector Network Analyzer

-Permittivity measurement software

-Sample placed in a waveguide shim

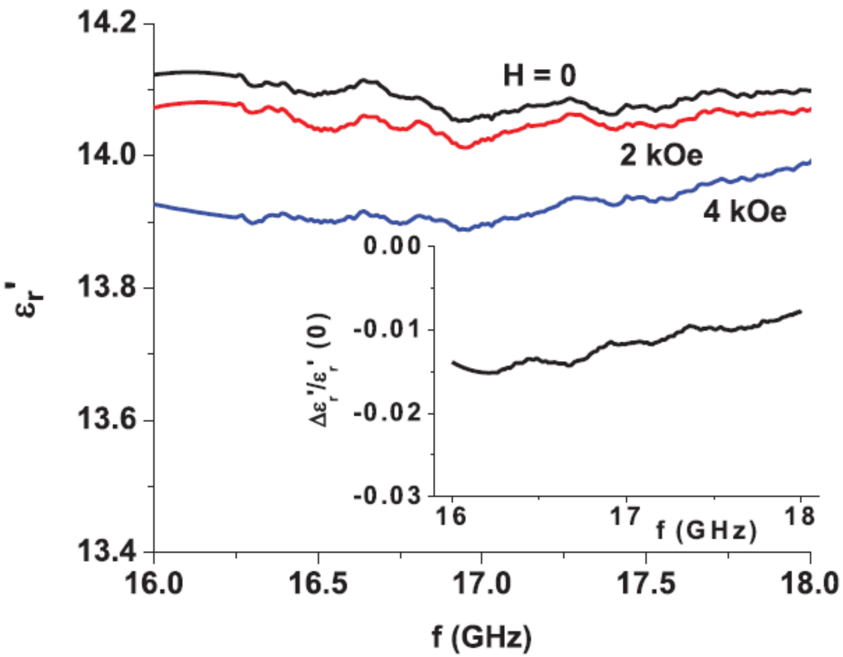
-Measurement of S_{11} and S_{12}

–ε estimated

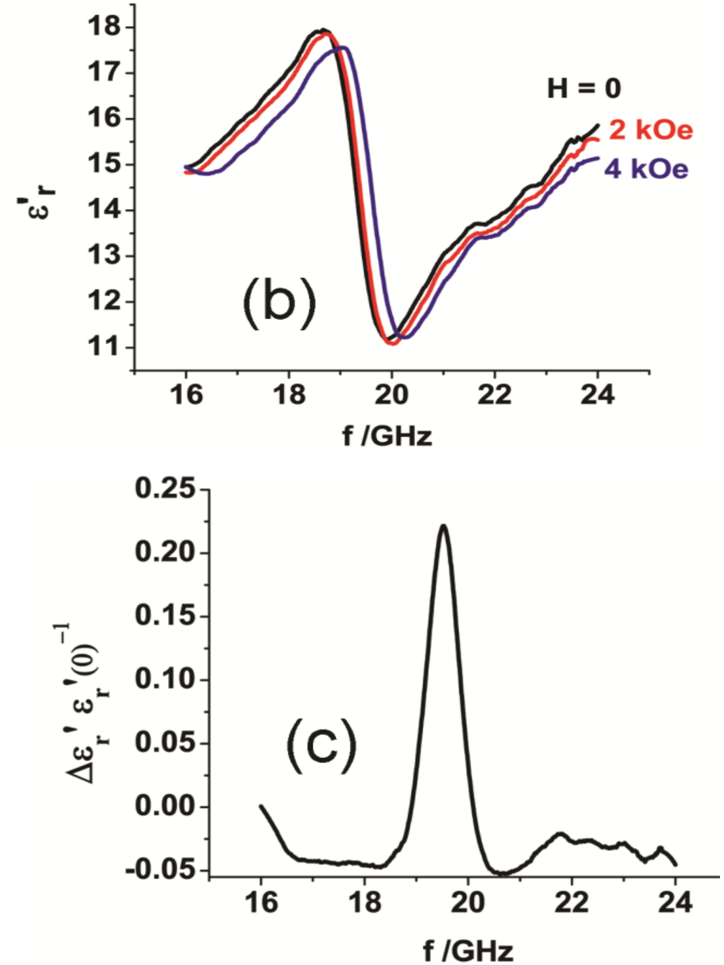


AIP Adv. 4, 097117 (2014)

MDE (off-resonance)



MDE (at resonance)



The H-induced change in the dielectric constant at 16-24 GHz:

Δ ε' / ε' (0) ~ - 5% to+23%.

AIP Adv. 4, 097117 (2014)

Chemical assembly: Summary

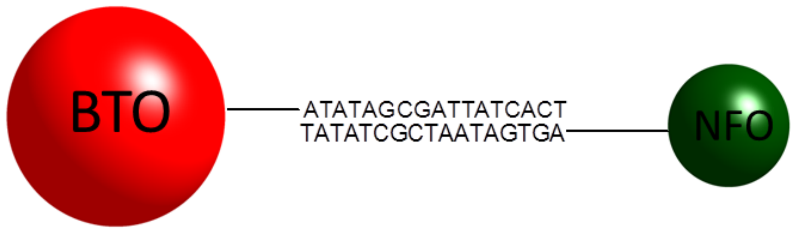
Core-shell nanoparticles of BTO and nickel ferrite were synthesized by "click-reaction" assisted self assembly.

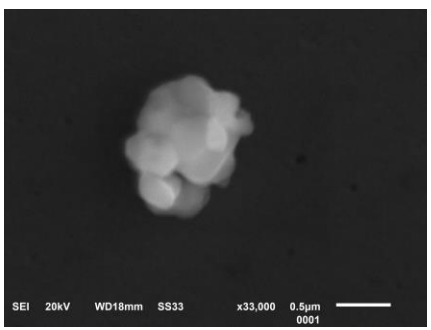
Linear chains and 2D/3D arrays of the particles assembled in a magnetic field.

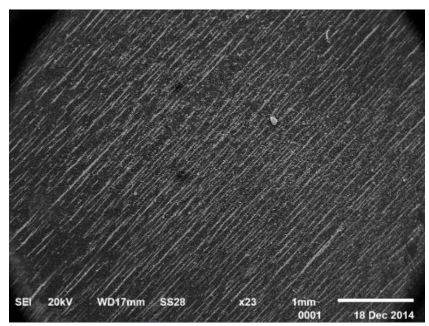
Magneto-electric coupling studied over 1 mHz-42 GHz reveal strong strain mediated cross-coupling in H-assembled samples.

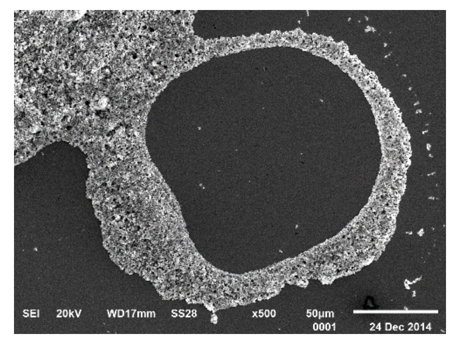
Models were developed for H-assembly, low-frequency ME coupling and magneto-dielectric effect in the microwave and mm-wave frequencies.

II. Core-Shell Nanocomposites Through DNA-DNA Hybridization and Magnetic Field Assisted Assembly into Superstructures









ferrite-ferroelectric core-shell particle **Further assembly into linear arrays and rings by H-assisted assembly**

Outline:

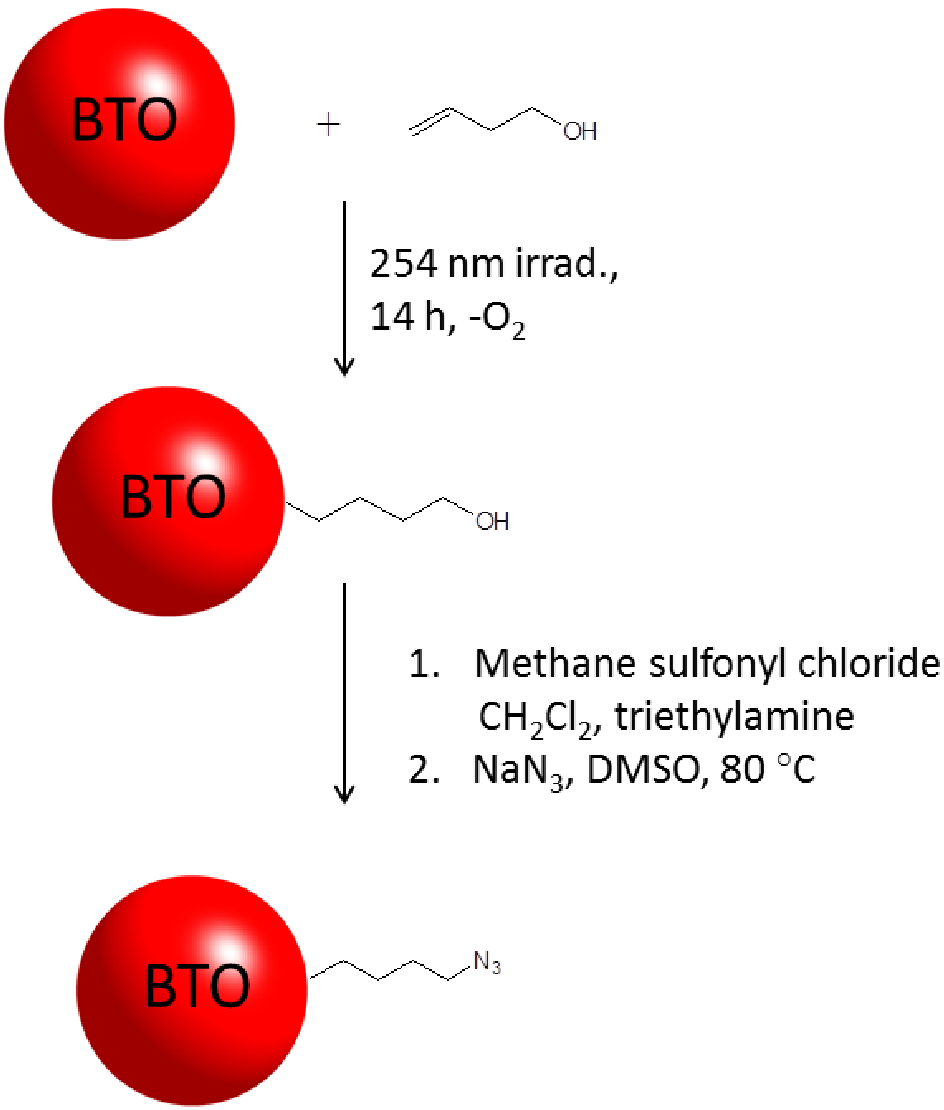
Assembly of BTO-NFO core-shell particles by functionalized DNA.

- **Attach azide group to BTO and NFO**
- **Use of click reaction to attach alkyn functionalized DNA1 to NFO and DNA 2 to BTO**
- **Assemble the core-shell particle by DNA hybridization**

SEM and SMM of particles and assembly

Assembly of superstructures in a magnetic field

Step 1: Attach azide groups to nanoparticles



$NiFe_2O_4$, (NFO) 200nm (1 g) and $BaTiO_3$, (BTO) 600nm (1 g).

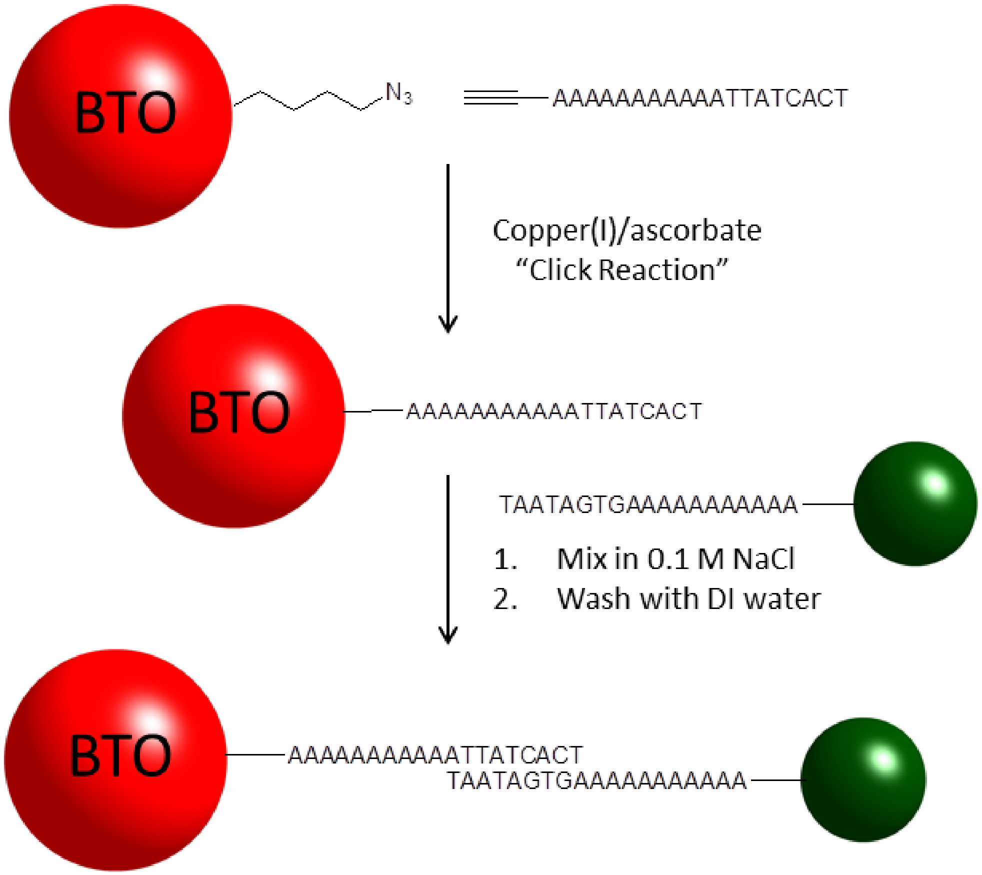
Add 3-Buten-1-ol was added under nitrogen.

irradiated with a UV light source (254 nm, ~15 mW/cm^2) to graft the 3-buten-1-ol molecules to the nanoparticle surface via the alkene group.

The terminal –OH groups were converted to methanesulfonyl (mesyl) groups which were subsequently converted to azide groups.

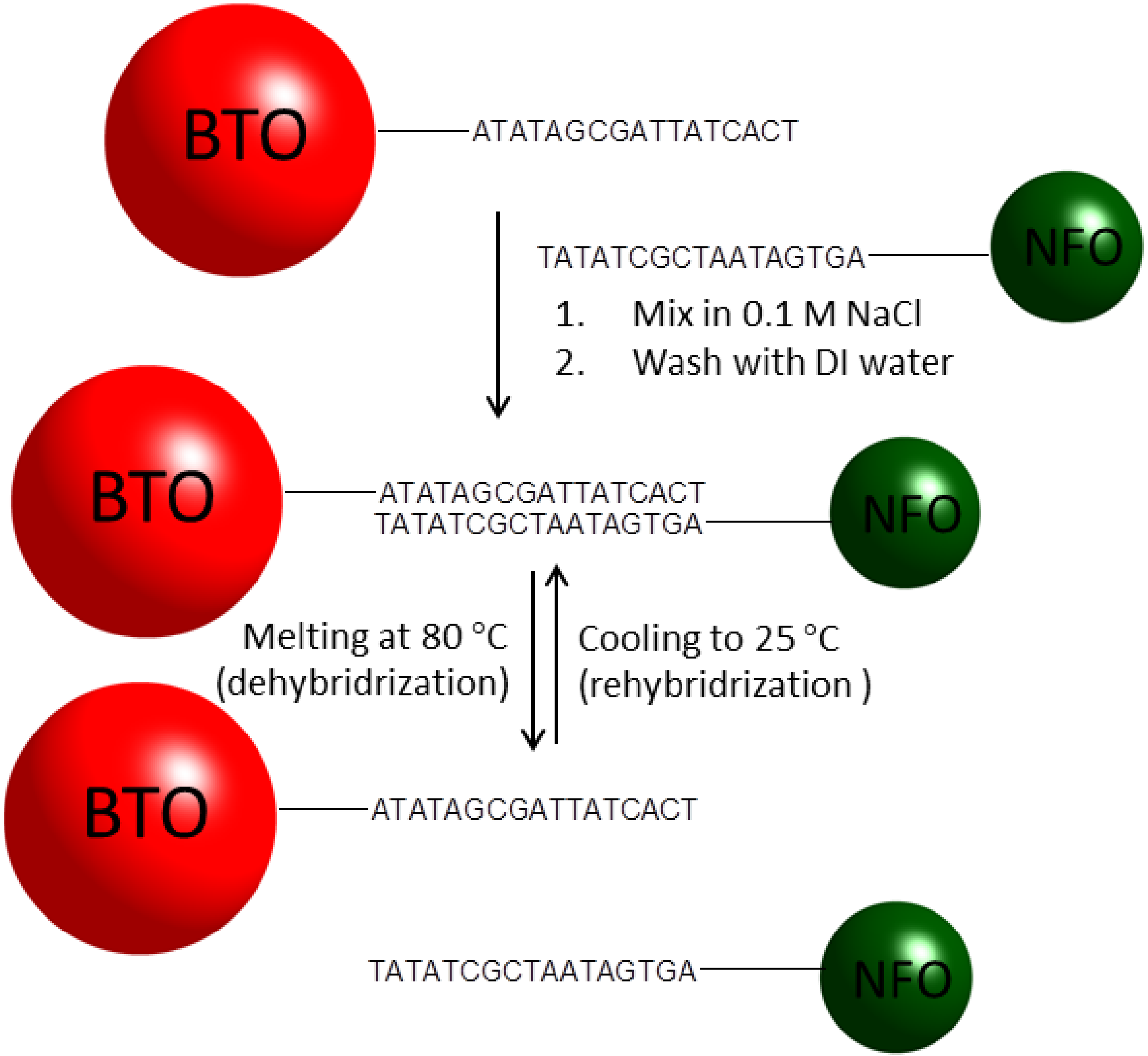
Step 2:

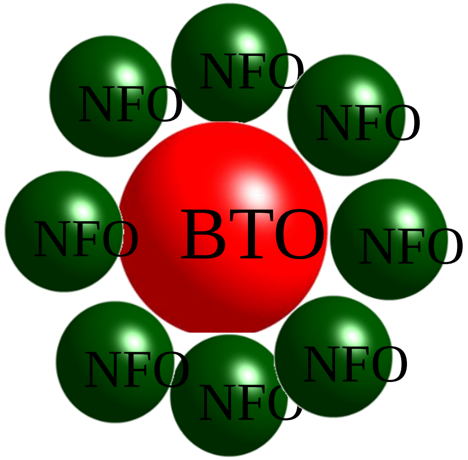
“click” methodology to covalently attach alkyne functionalized oligomeric DNA (ODN 1 and ODN 2) to azide-functionalized nanoparticles.



One vial of complimentary alkyne-functionalized DNA was added to a flask containing each azide functionalized nanoparticle.
Add copper acetate and ascorbic acid.

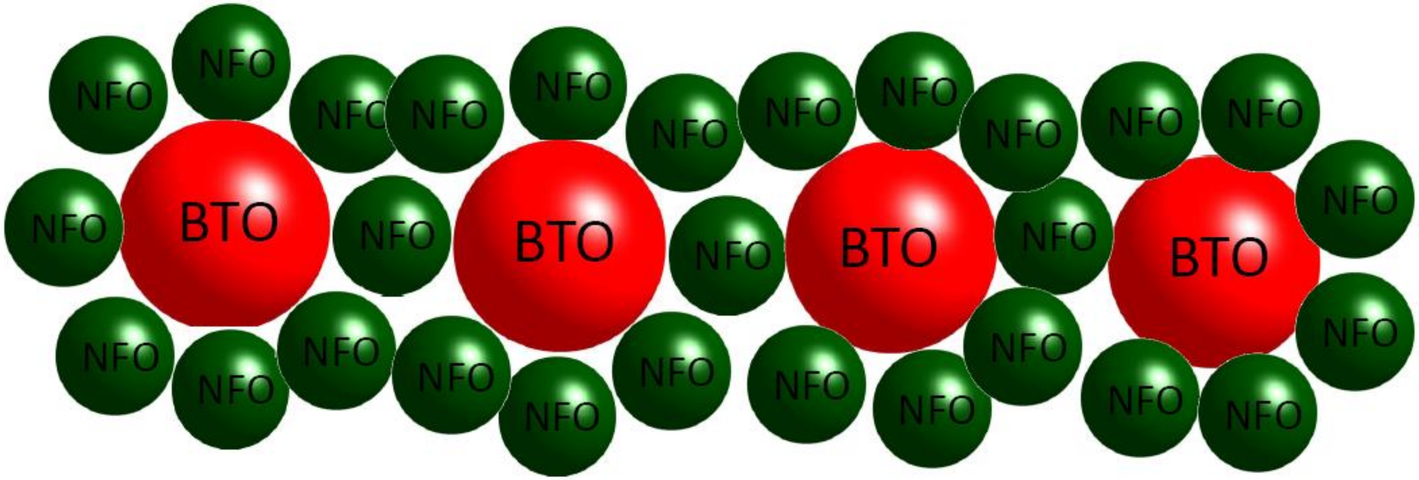
Step 3: Assembly of core-shell particles



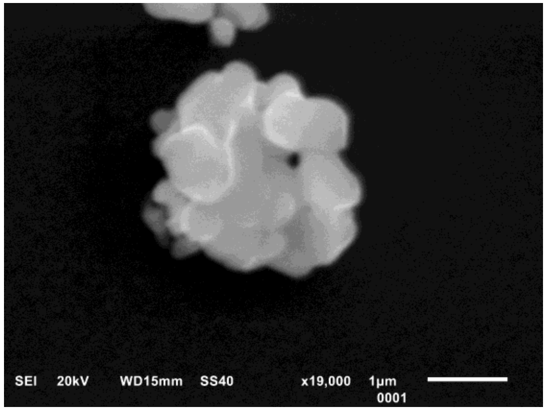


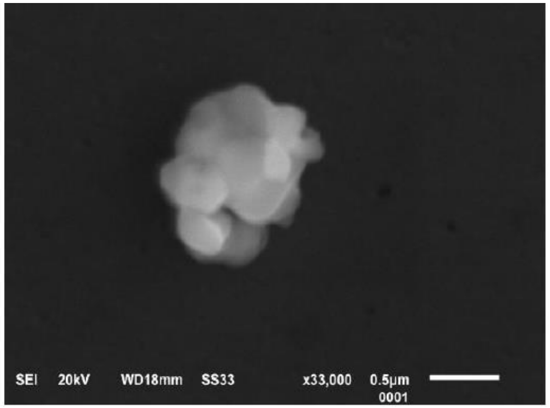
Core-Shell Assemblies

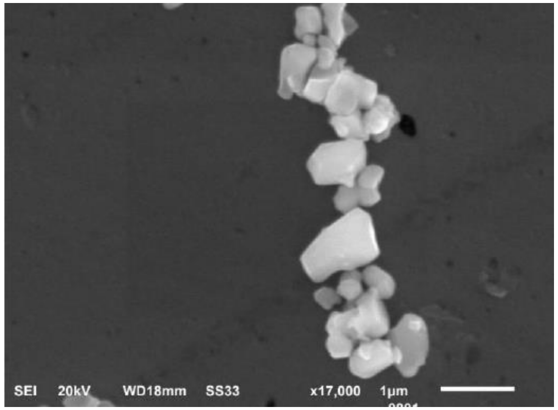
H-assisted assembly of core-shell particles

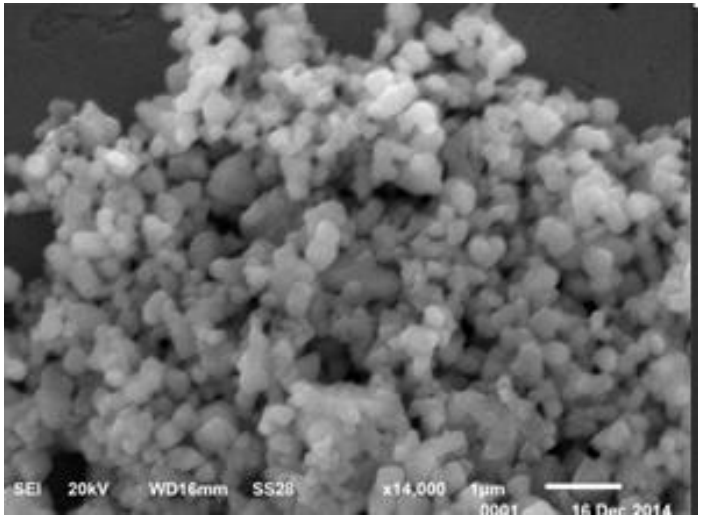


As-assembled composites of NFO (200 nm) and BTO (600 nm) mixed in a 1:1 ratio.

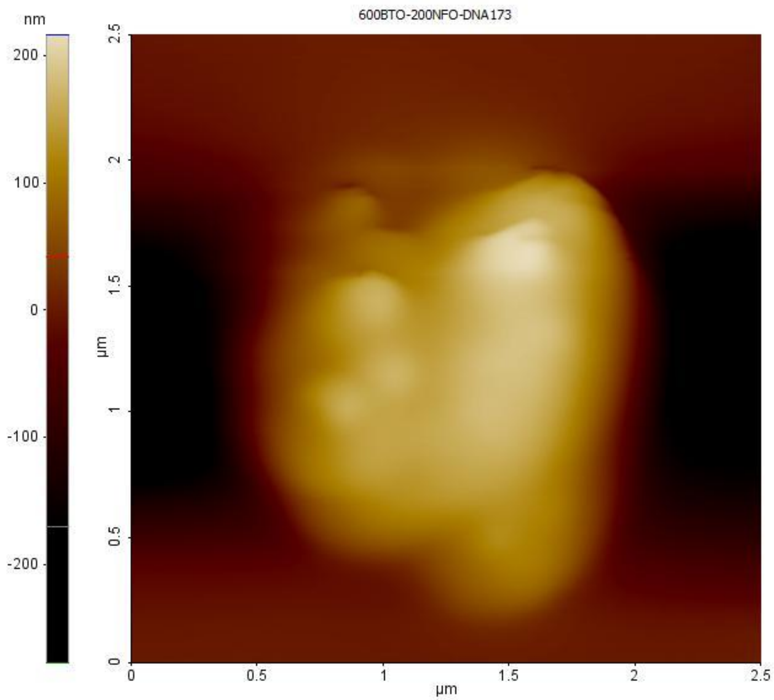


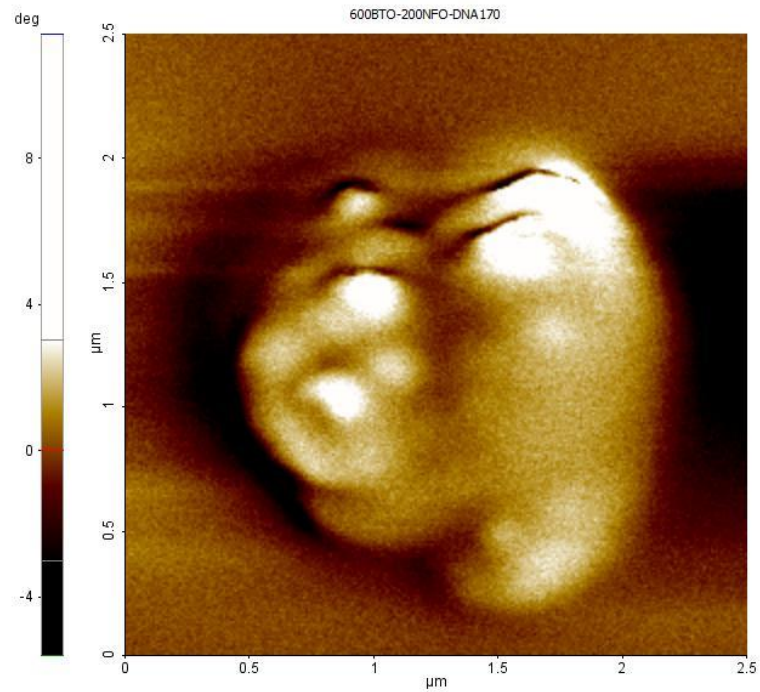






Magnetic Force Microscopy of Single 600 nm BTO -200 nm NFO Core-Shell Particle

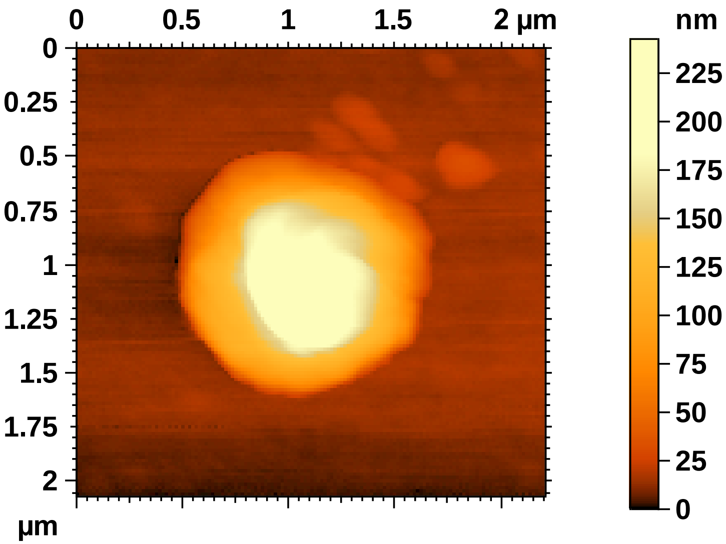




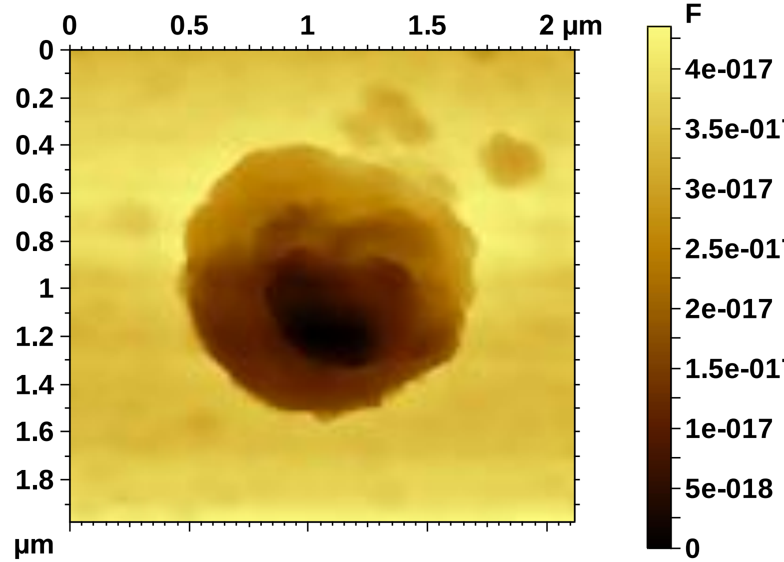
MFM Topography Image

MFM Phase Image

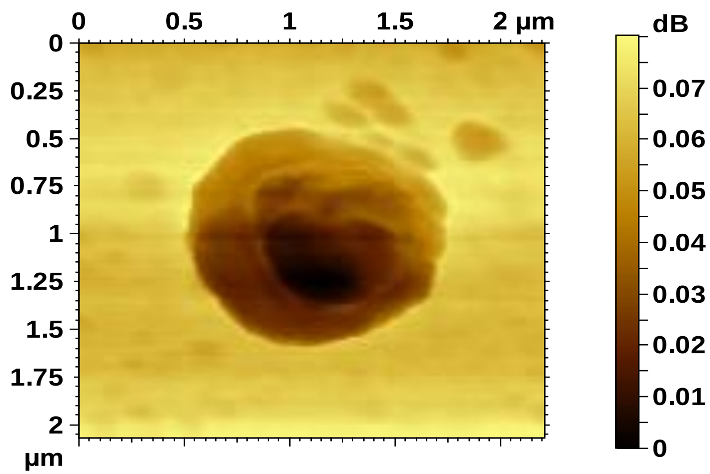
Scanning Microwave Microscopy of cluster of 600 nm BTO-200nm NFO core-shell particle cluster



AFM topography



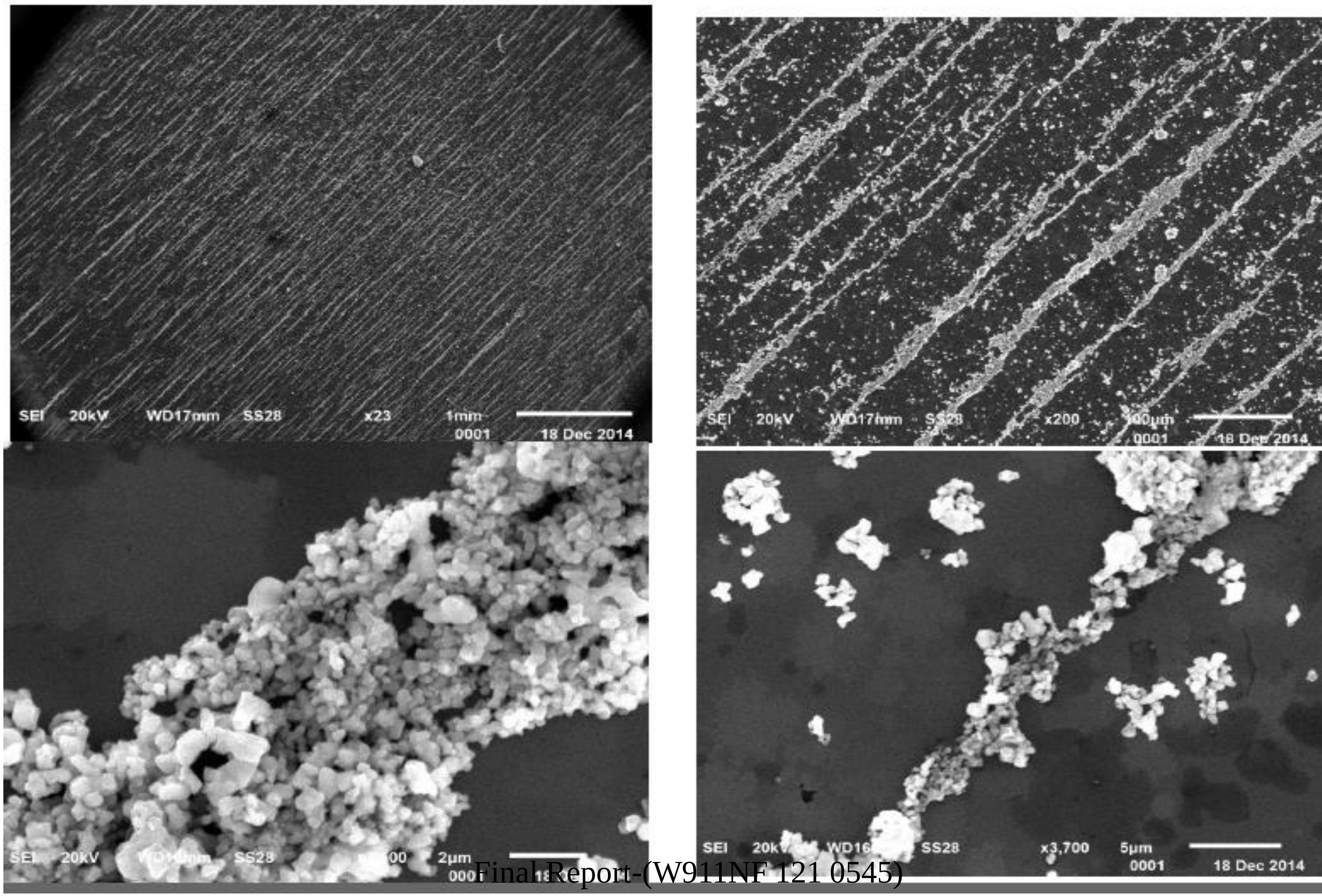
Capacitance image at 14



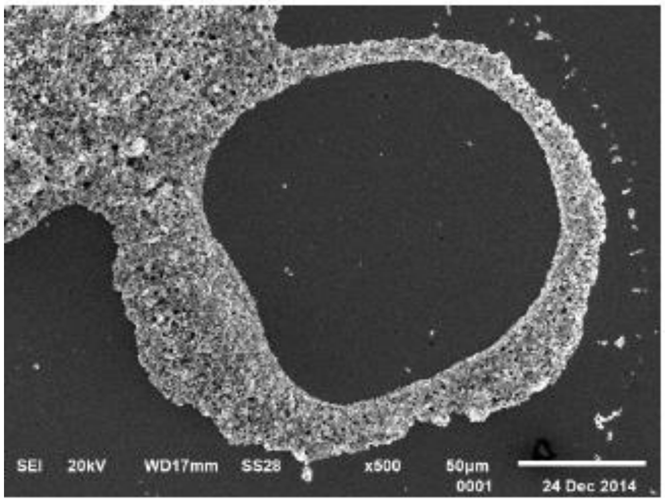
5)

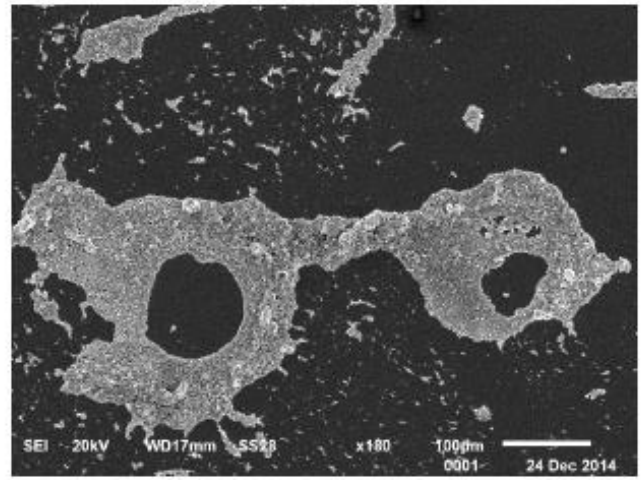
S11 amplitude image at 14 GHz

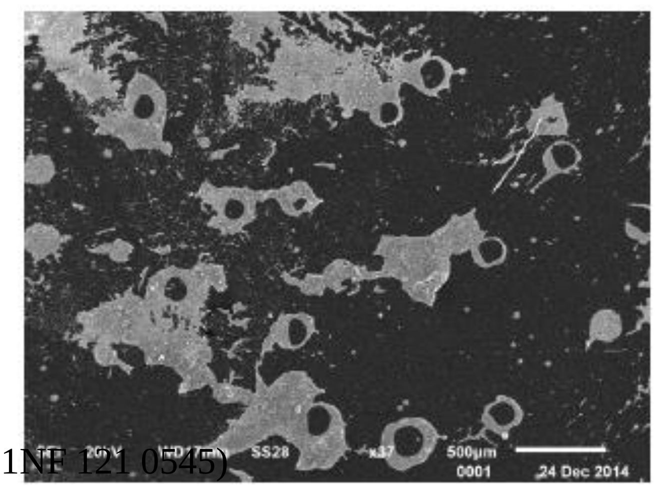
Mixtures of NFO (200 nm) and BTO (600 nm) composites 1.5:1 heated to 80 ºC and allowed to cool to room temperature in a uniform magnetic field



Mixtures of NFO (200 nm) and BTO (600 nm) composites 1.5:1 heated to 80 ^{o}C and allowed to cool to room temperature in a rotating magnetic field







ME characterization

ME characterization on pressed pellets of as-assembled core-shell composites was done by :

(i) static magnetic field H induced polarization P and
(ii) low frequency ME voltage coefficient measurements.

Following this the disks were annealed at high temperatures so that the samples are free of DNA and other coupling agents and the ME measurements were carried out on them.

For comparison we measured the ME interaction strengths in bulk composites prepared by mixing NFO and BTO nanoparticles to form bulk composites with random distribution of the ferroic phases.

H-induced Polarization – DNA assembled samples

- Data for as-assembled and annealed samples

- Change in Pr measured from P vs E under H

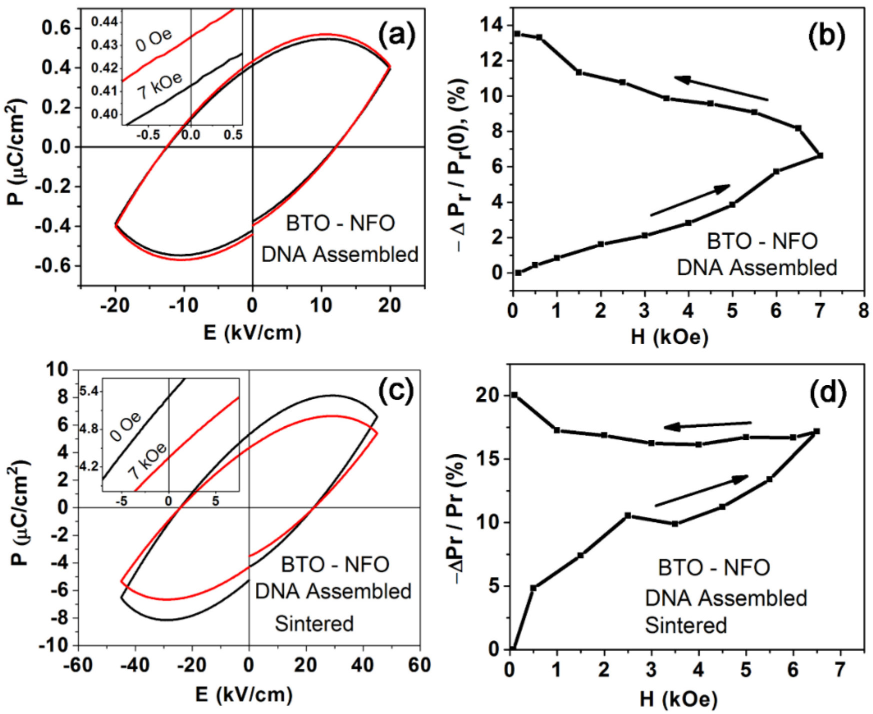
- Pr decreases under static magnetic field

– $\Delta P_r / P_r (H=0) = [P_r(H)-P(H=0)] / P_r (H=0)$ is shown as a function of H

- Data on ΔPr shows hysteresis

– $\Delta P_r / P_r$ = 14 % for unannealed sample

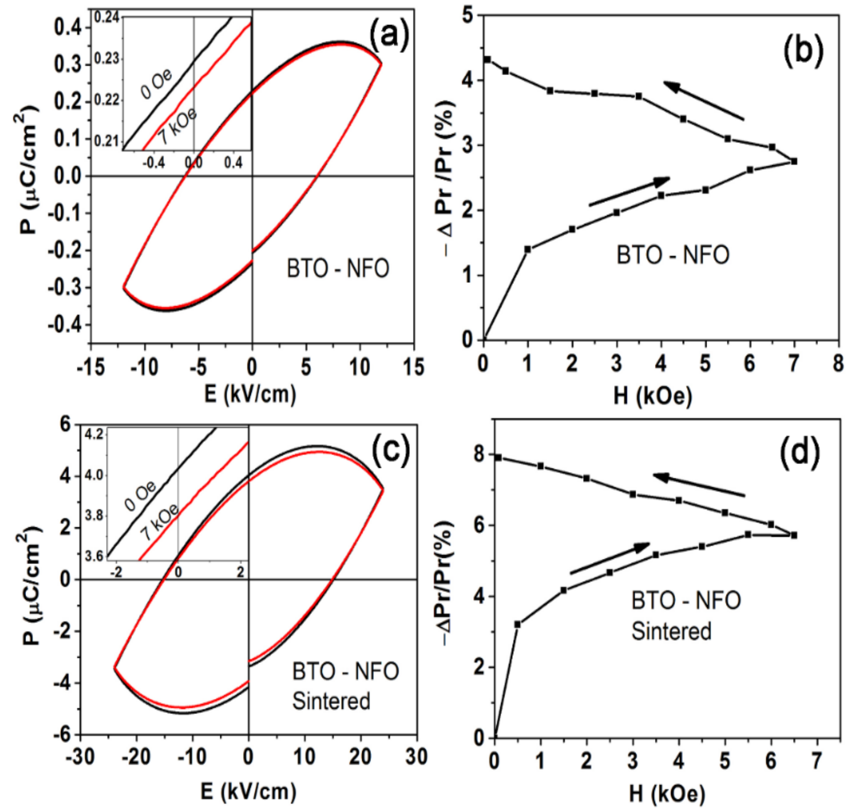
- 20% for annealed sample.



H-induced Polarization – Bulk composite

- Prepared by mixing 200 nm NFO and 600 nm BTO particles (random distribution of the two phases).

- Discs of pressed and annealed samples



- Pr decreases under static magnetic field

– ΔP_r / P_r (H=0) is shown as a function of H

- Data on ΔPr shows hysteresis

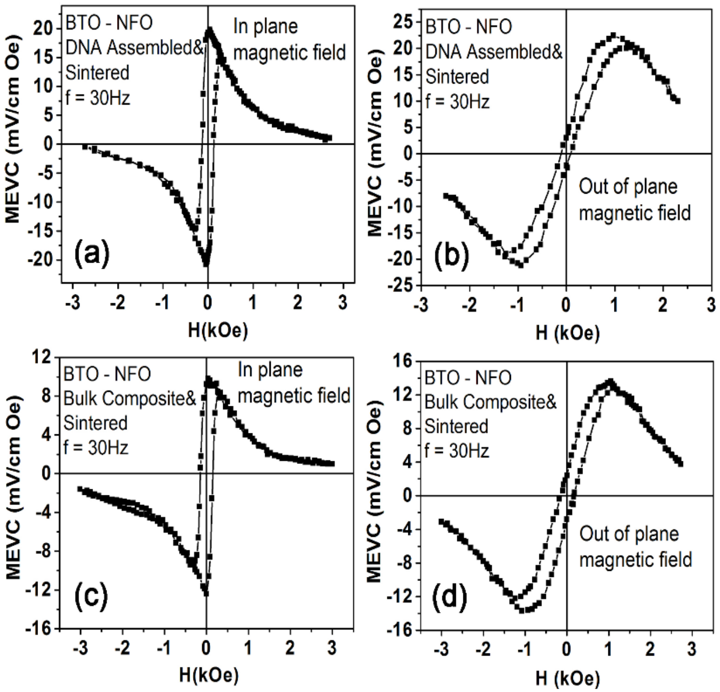
– ΔP_r / P_r = 4 % for unannealed sample

- 8% for annealed sample.

- Much smaller change compared to DNA-assembled samples.

Low-frequency ME voltage coefficient

- MEVC measurements on sintered discs of NFO-BTO composites.
- Samples were first poled in E = 1 kV/cm at room temperature
- Subjected to a DC bias magnetic field H and an ac field of H_{ac} = 1 Oe at 30 Hz.
- ac and dc magnetic fields were parallel to each other and applied either parallel or perpendicular to the disc plane.
- The ME voltage induced across the disk thickness was measured as a function of H and field orientations.



- MEVC shows a zero-bias value of 20 mV/cm Oe
- indicative of a built-in magnetic field arising due to dipole-dipole interactions between NFO particles in the core-shell structures.
- With increase in H, MEVC decreases and the coupling vanishes at H = 2 kOe due to saturation of magnetostriction resulting in zero value for the piezomagnetic coupling q.
- A hysteresis is also seen in MEVC vs H data.

- DNA assembled sample shows a factor 2 higher MEVC than bulk composite

Smmary

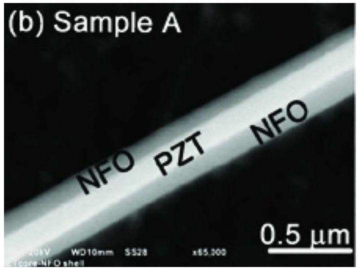
Ferrite-ferroelectric core-shell particles were assembled using DNA hybridization.

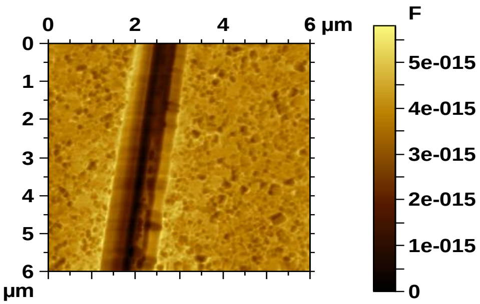
The availability of custom-designed DNA allows for control over the strength and specificity of interaction between nanoparticles.

The advantage of this method for assembling nanoparticle composites is that one can disassemble the composites and reassemble them under various conditions.

DNA-assembled samples show strong ME interactions.

III. Ferrite-Ferroelectric Core-Shell Nanofibers by electrospinning and Studies on Magneto-electric Interactions





Appl Phys Lett 104, 052910 (2014)

Outline

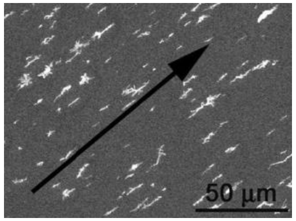
-Synthesis of nickel ferrite/ Barium titanate or PZT core-shell fibers by electrospinning

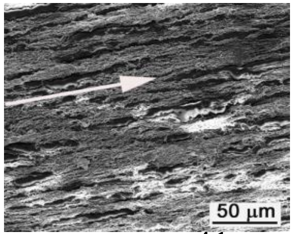
-Characterization by SEM, XRD, MFM

-Ferromagnetic characterization -- Magnetization and FMR

-Ferroelectric order parameters: P vs E

- Assembly in a magnetic field: uniform and non-uniform fields



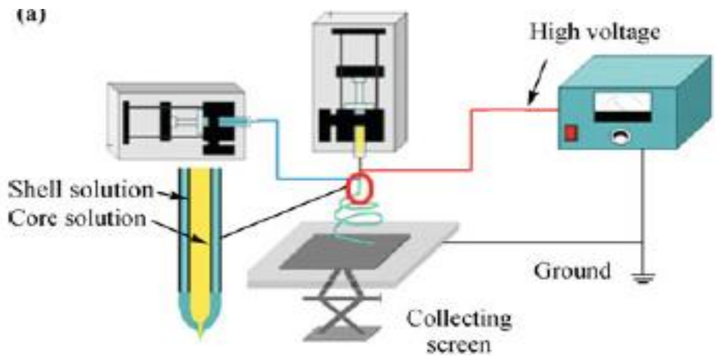


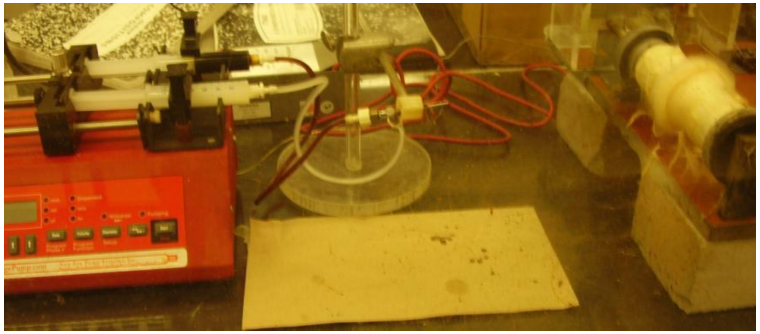
-ME characterization: P vs E under H
ε vs f (20-22 GHz)
Low-frequency ME voltage
E-tuning of FMR

Nanowire synthesis

Procedure

-preparation of ferrite $NiFe_2O_4$ (NFO) and Ba TiO_3 or PZT: Pb $Zr_{0.52}$ $Ti_{0.48}$ O_3
-Electro-spinning by dispensing the sol with a dual syringe pump and a coaxial needle
-V = 15-20 kV
-Fiber collected on a rotating drum





<u>**Nickel ferrite – BTO or PZT nanowires**</u>

***Sample A*: BTO or PZT core and NFO shell**

***Sample B*: NFO core and BTO or PZT shell**.

BTO/NFO fibers

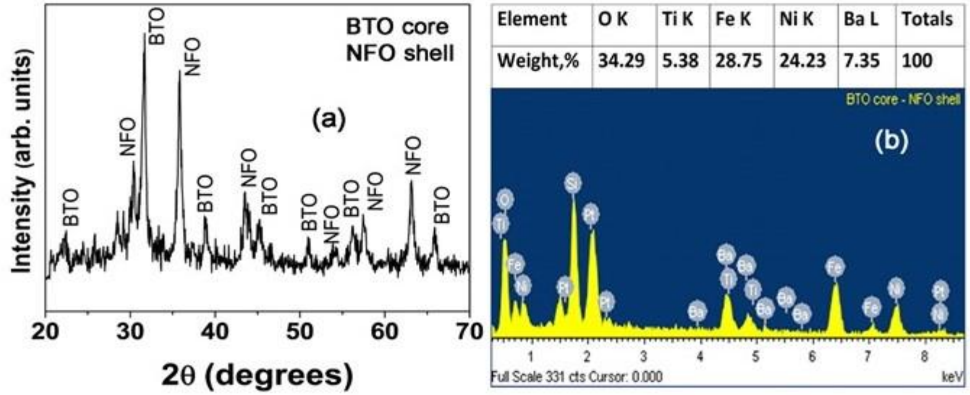
<u>Sample A:</u>

BTO core dia ~ 250 nm;
shell thickness~125 nm
Ferrite volume 75%

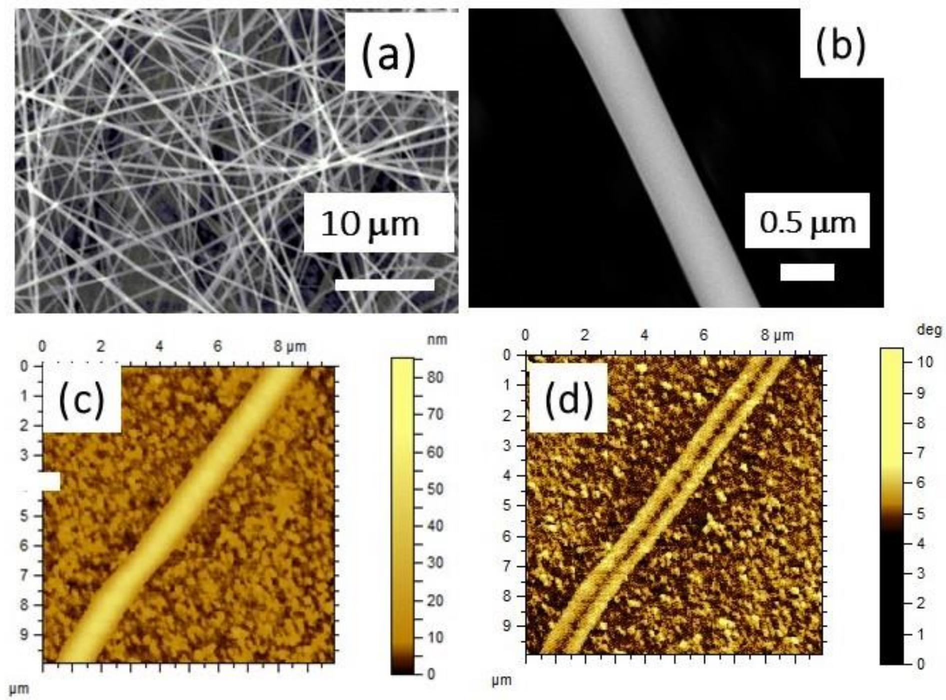
<u>Sample B</u>:

Ferrite core dia ~ 500 nm
Shell thickness 500 nm

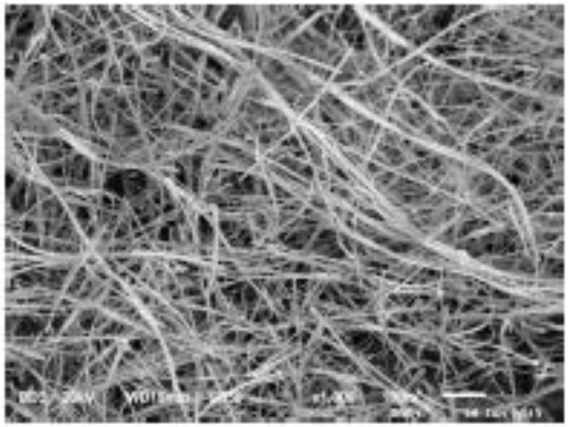
Ferrite volume 12%

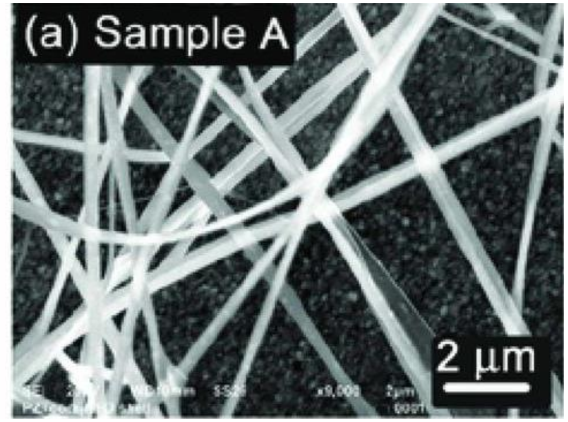


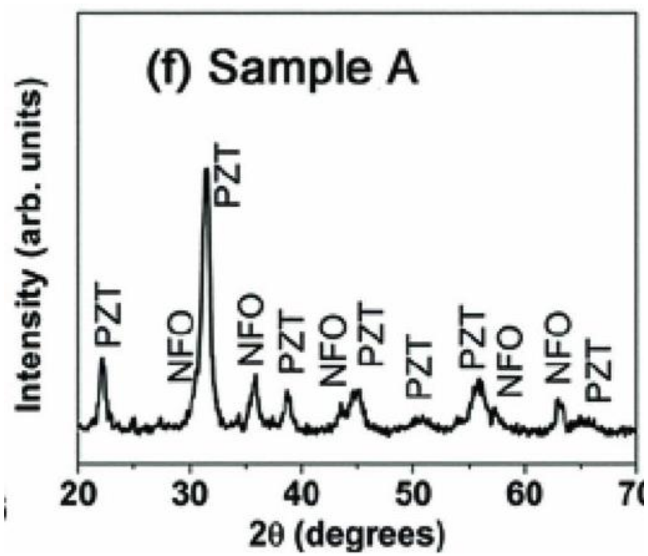
Element	O K	Ti K	Fe K	Ni K	Ba L	Totals
Weight,%	34.29	5.38	28.75	24.23	7.35	100



PZT/NFO fibers: Structural Characterization: SEM and XRD





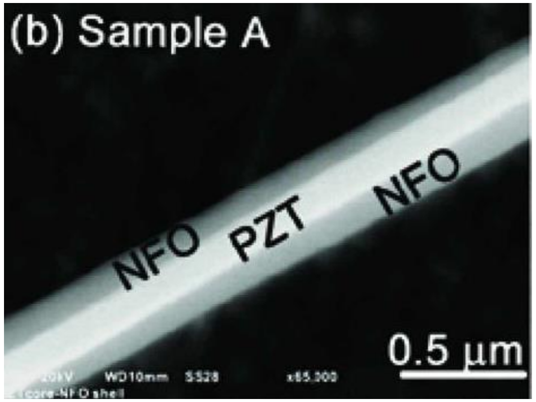


X-ray Diffraction for Annealed fibers (650-700C)

Uniform fibers of length 10-30 μm

Free of impurities

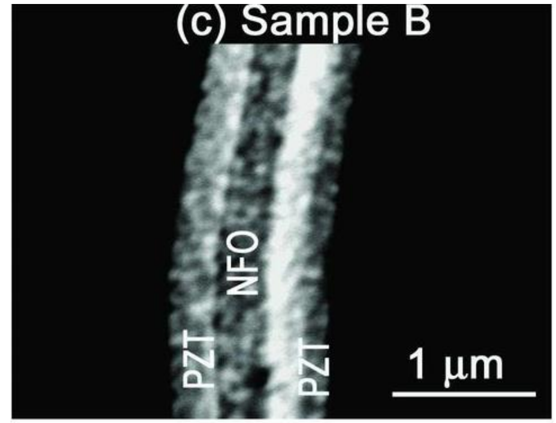
PZT/NFO feibers: SEM of individual fibers



Core (PZT) dia. = 200 nm

Shell (NFO) thickness = 125 nm

Ferrite volume ~ 80%
PZT vol.   ~ 20%



Core (NFO) dia. = 450 nm

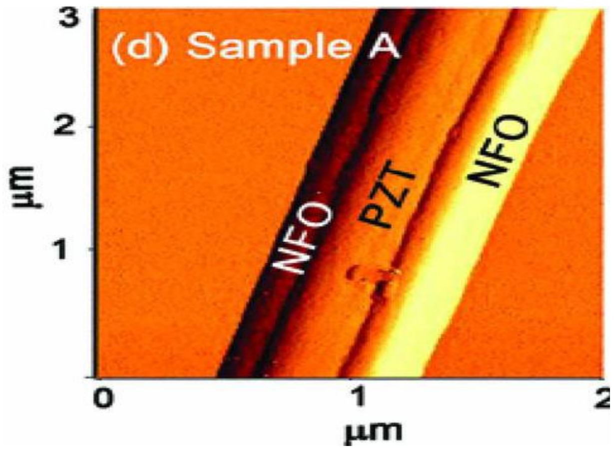
Shell (PZT) thickness = 175 nm

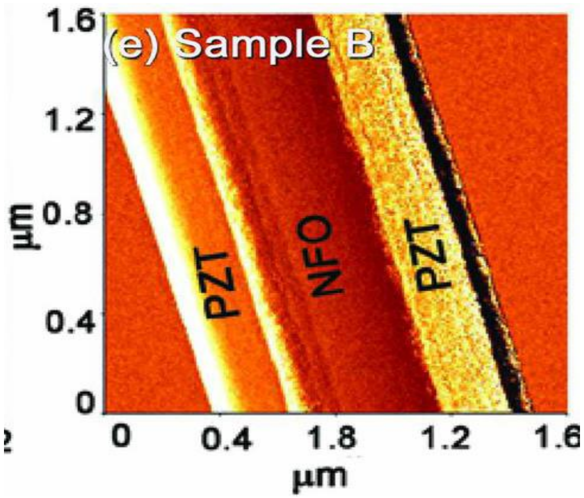
Ferrite vol. ~ 32%
PZT ~ 68%

Magnetic Force Microscopy (MFM)

Park Systems XE-100E

MFM phase image shows NFO and PZT in different contrast





BTO/NFO fibers: Ferroelectric and ferromagnetic characterization

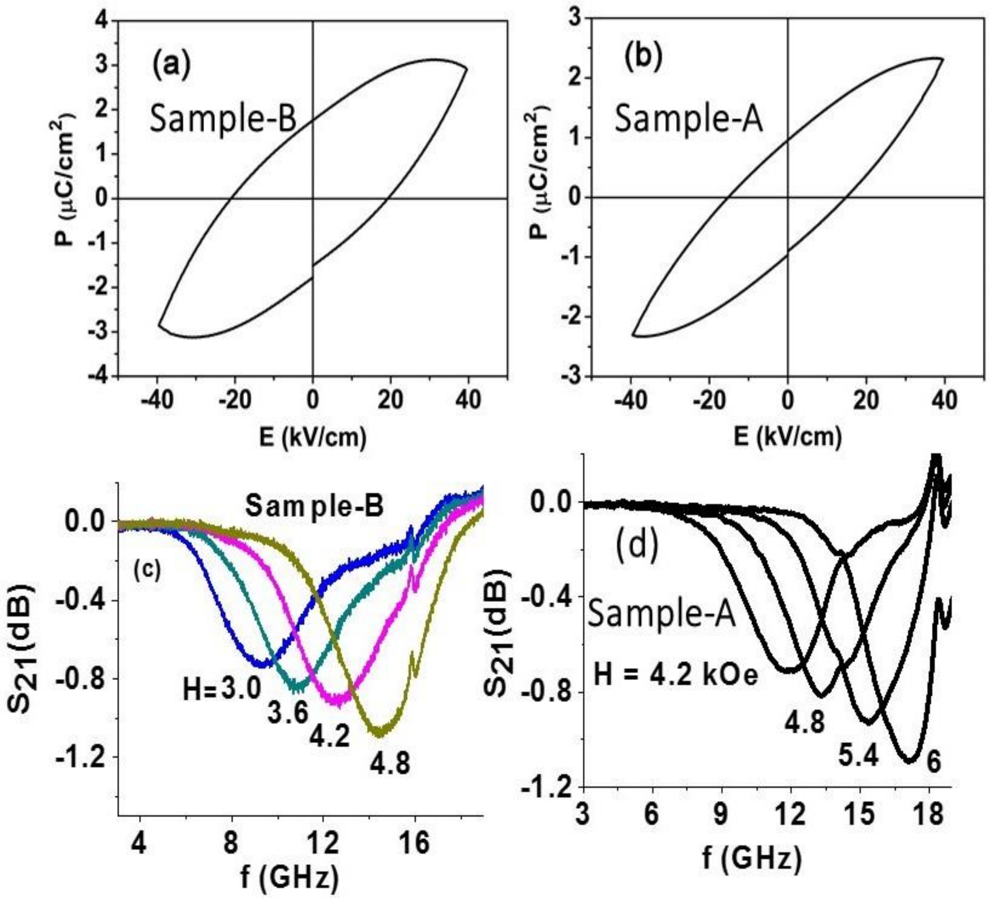
$P_r = 1\text{ -}2\ \mu C/m^2$

Sample-A
$\gamma = 3.1$ GHz/kOe and $4\pi M_{eff} = 480$ G

Ferrite volume 75%
Ferrite-only $4\pi M \sim 0.65$ kG
High anisotropy field
-

Sample-B:
$\gamma = 3.1$ GHz/kOe and $4\pi M_{eff} = 400$ G

Ferrite volume 12%
Ferrite-only $4\pi M \sim 3.3$ kG



PZT/NFO: Ferromagnetic order parameters: Magnetization and FMR

M Measured with a Faraday Balance (at room temperature).

Both samples are ferromagnetic

ample A:

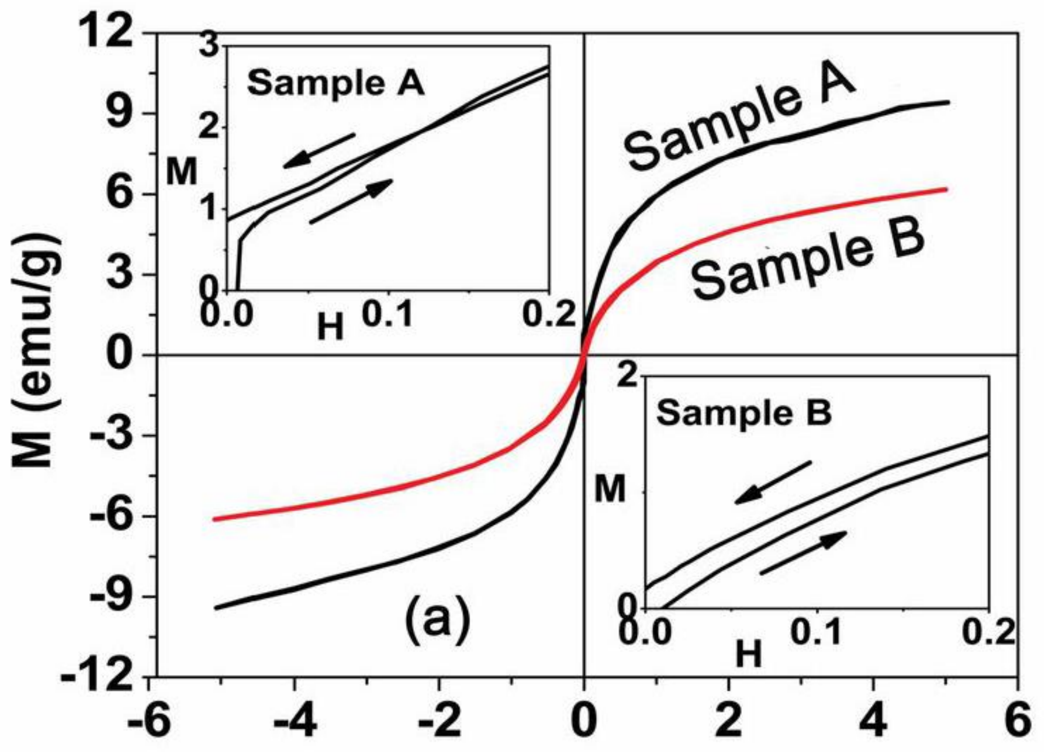
M_s = 9.6 emu/g
-Small compared to bulk NFO

Sample B:

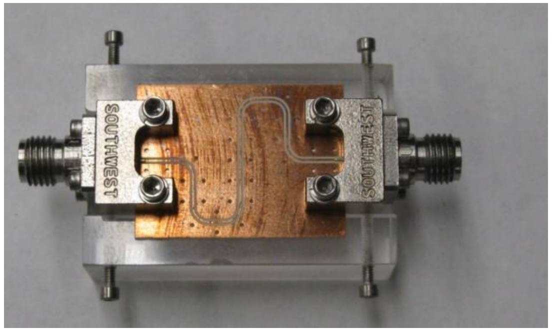
M_s = 6.5 emu/g

Ferrite-only M smaller than for for nickel ferrite.

High magnetic anisotropy field in both fibers.



PZT/NFO: Ferromagnetic resonance



-Using a coplanar slot line transducer

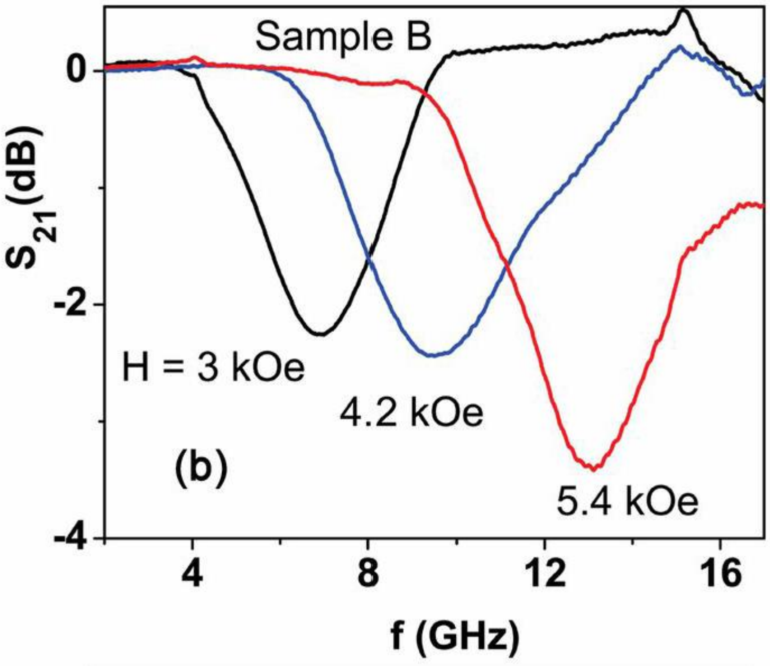
-S_{21} vs f profiles for a 5 mm x 2 mm x 0.5 mm sample

-H parallel or perpendicular to sample plane

3-db width ~ 4-6 GHz
Line-width ~ 1.4 -2 kOe

γ = 2.8 GHz/kOe (g =2.0)
$4\pi M_s$ (effective) = $4\pi M_s + H_a$

$4\pi M$ = 500 G
H_a = 300 Oe



PZT/NFO: Ferroelectric characterization

P vs E

3 orders of magnitude smaller P-value compared to thin films.

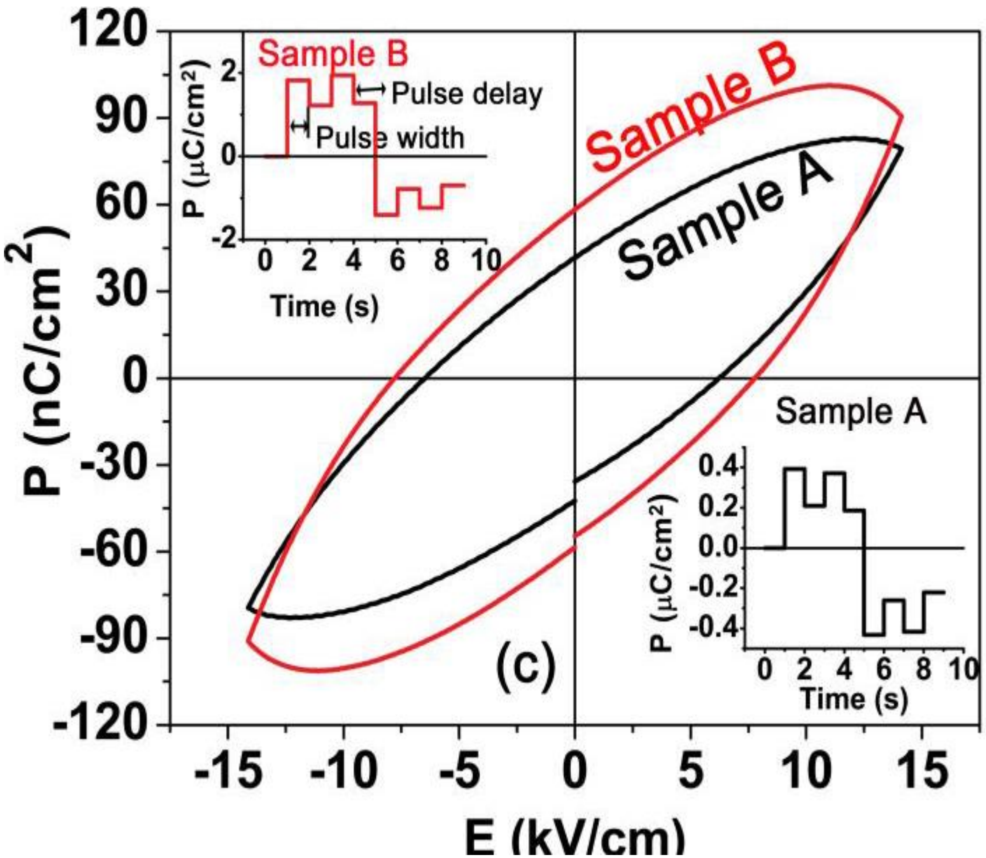
Sample A:

$P_r = 44\ nC/m^2$

Sample B:

$P_r = 58\ nC/m^2$

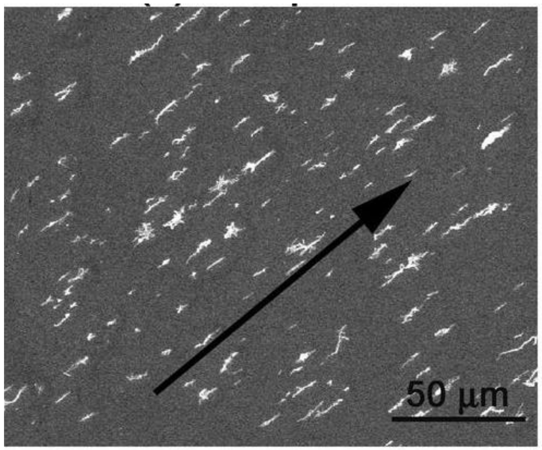
PUND data shows switchable polarization



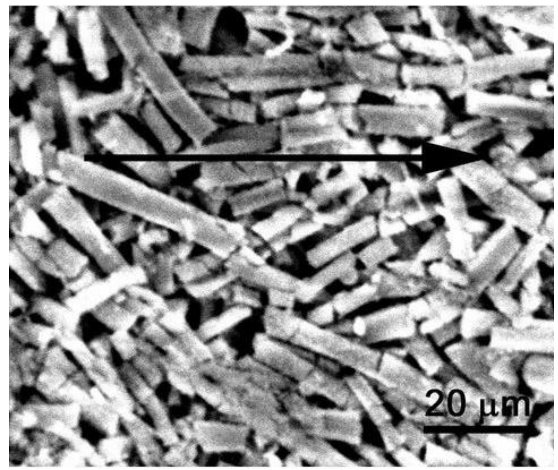
Magnetic field directed self-assembly

Assembly in Uniform magnetic field

(solenoid or electromagnet)
assemble the fibers into uniform chains



Fibers on a glass slide

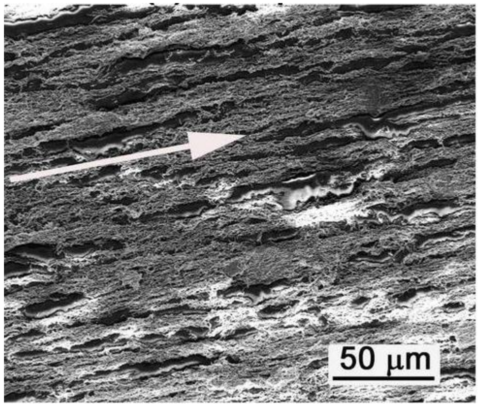


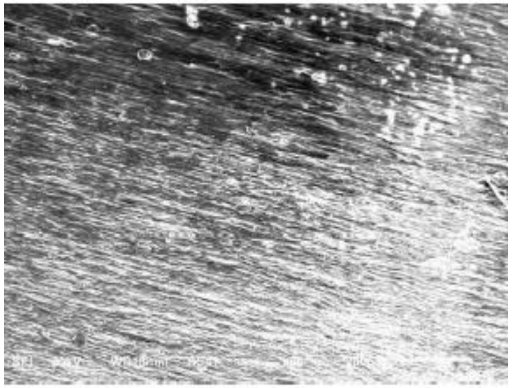
Disc of fibers pressed in H

Non-uniform field (permanent magnet)

Field gradient ~ 400 Oe/cm

Exerts an attractive force on the fibers and align them toward the regions of high field strengths.





Magneto-electric Effects

-- Direct ME effects

H induced polarization

Magneto-dielectric effect

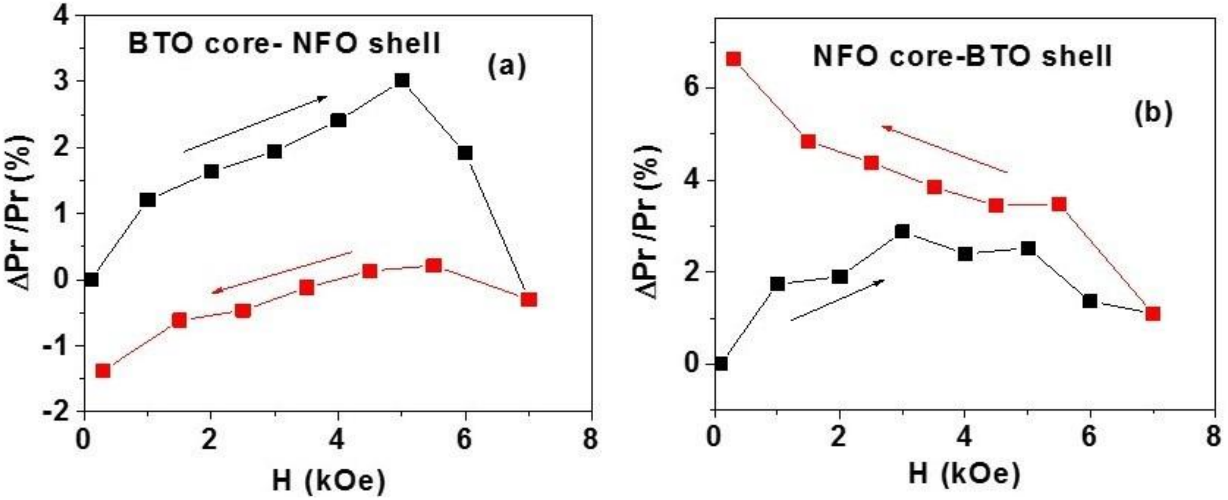
Low frequency ME voltage coefficient

- **Converse ME effect**
  - E-tuning of ferromagnetic resonance

H-induced polarization: BTO/NFO

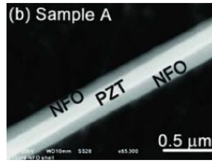
P vs E under H

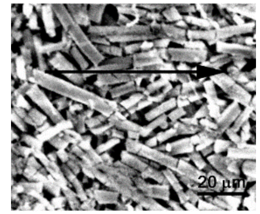
Fractional change in Pr vs H



PZT/NFO: H-induced polarization

Sample A



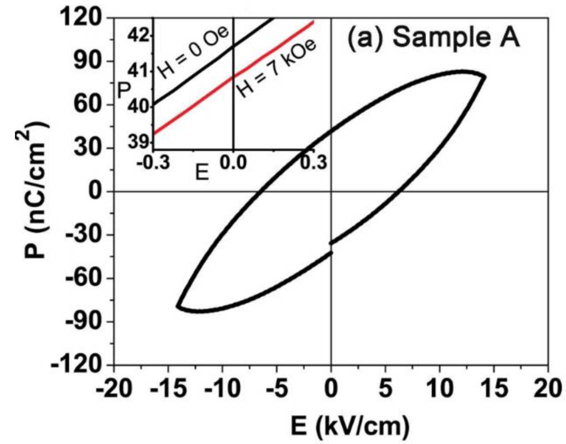


Disc pressed in uniform magnetic field.

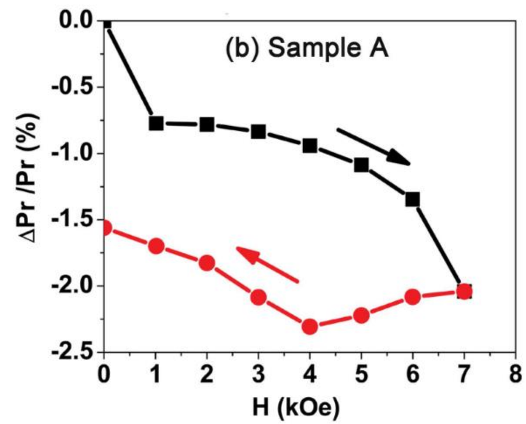
P vs E under H

Pr decreases with increasing H

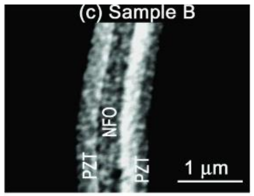
$\Delta P_r / P_r (H=0) = [P_r(H)-P(H=0)] / P_r (H=0)$

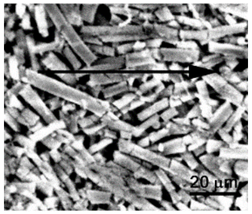


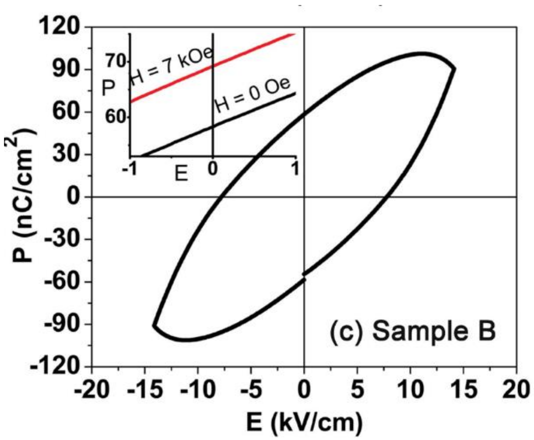
ΔP_r vs H show hysteresis



ME effect: H-induced polarization – Sample B





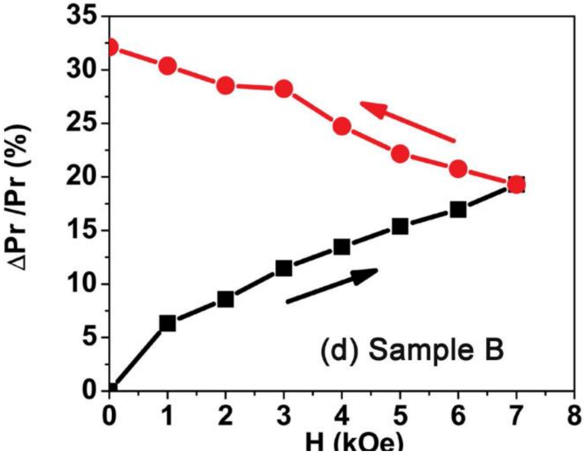


Pr increasing with increasing H

ΔP_r vs H show hysteresis

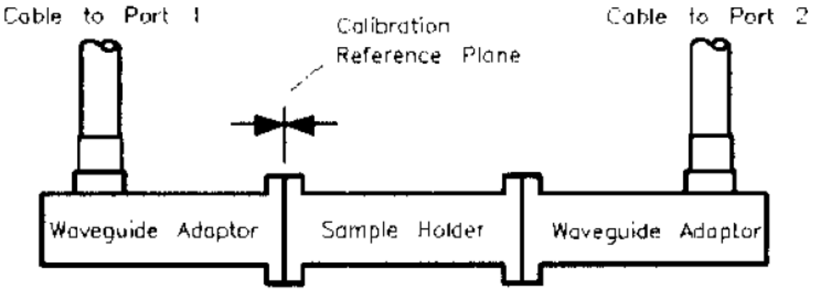
ΔP_r -positive for Sample B
 ΔP_r - negative in Sample A

Possibly due to compressive stress on PZT in one case and tensile stress n the other case



Magneto-dielectric effect: 20-22 GHz

H-induced variation in dielectric constant

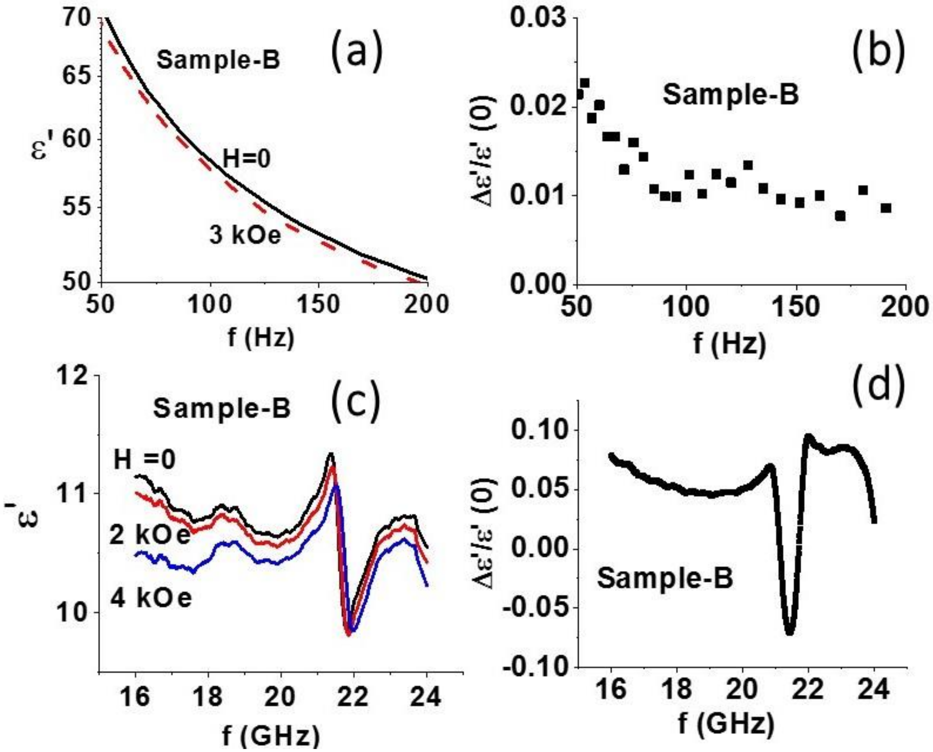


-Agilent Vector Network Analyzer
-Permittivity measurement software
-Film on a glass slide placed in a waveguide shim
-Measurement of S11 and S12
–ε estimated from S vs f data

MDE in BTO/NFO

-Measured in discs pressed in H

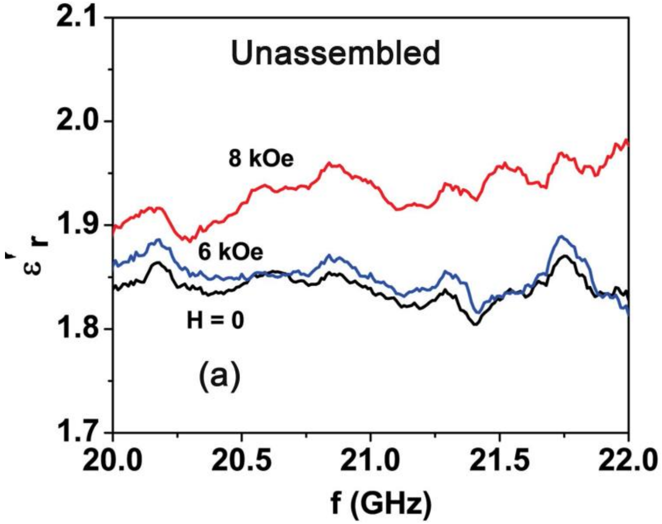
- Low frequency MDE

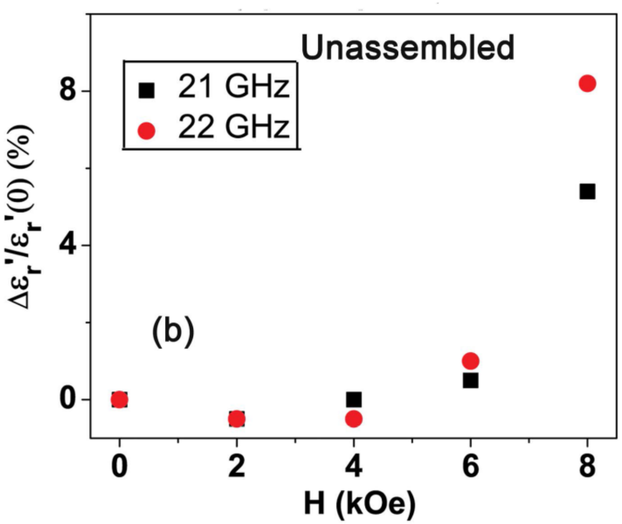


- MDE at dielectric resonance

Magneto-dielectric effect: PZT/NFO
Sample B

Unassembled film on glass

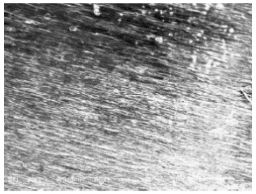


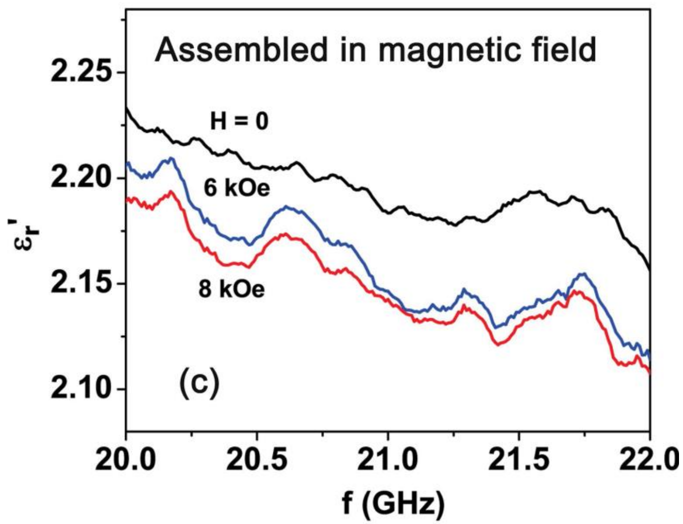


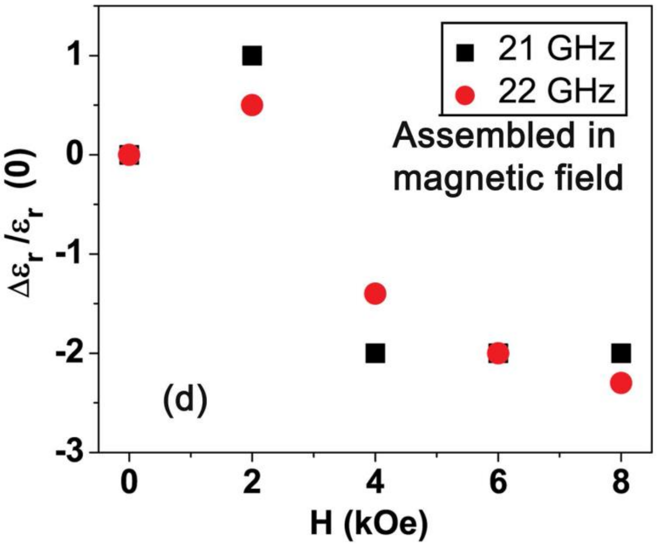
$\Delta\varepsilon_r'/\varepsilon_r'(0)=[\varepsilon_r'(H)- \varepsilon_r'(H=0)]/\varepsilon_r' (H=0)$

$\Delta\varepsilon_r'$ -positive and increases with H

MDE: Film assembled on glass slide – PZT/NFO Sample B



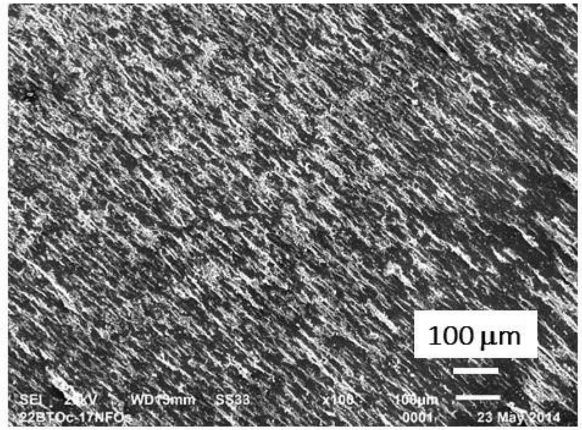


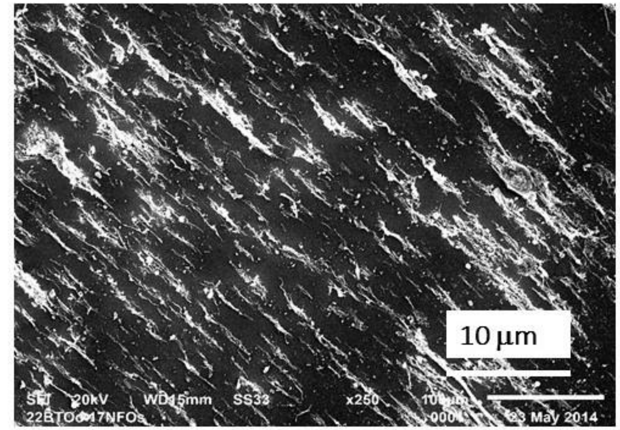


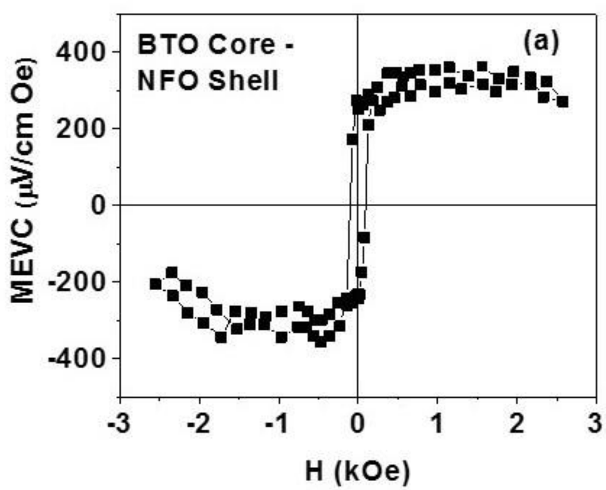
decreases with H

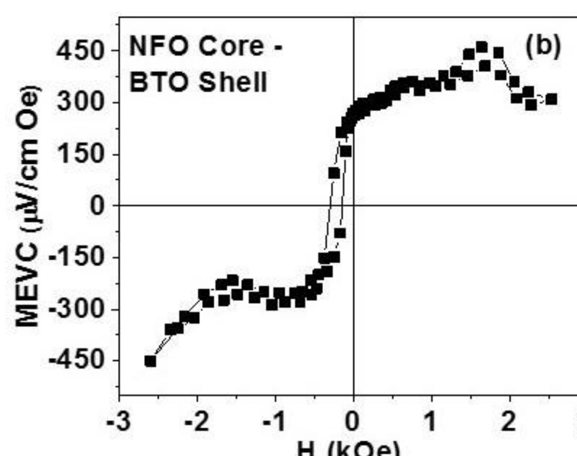
$\Delta\varepsilon_r$‘ shows a smaller change compared to films with randomly oriented fibers.

Low frequency ME effects in BTO/NFO









Low-frequency ME Voltage Coefficient: PZT/FO

Voltage response of the composite to applied ac magnetic field

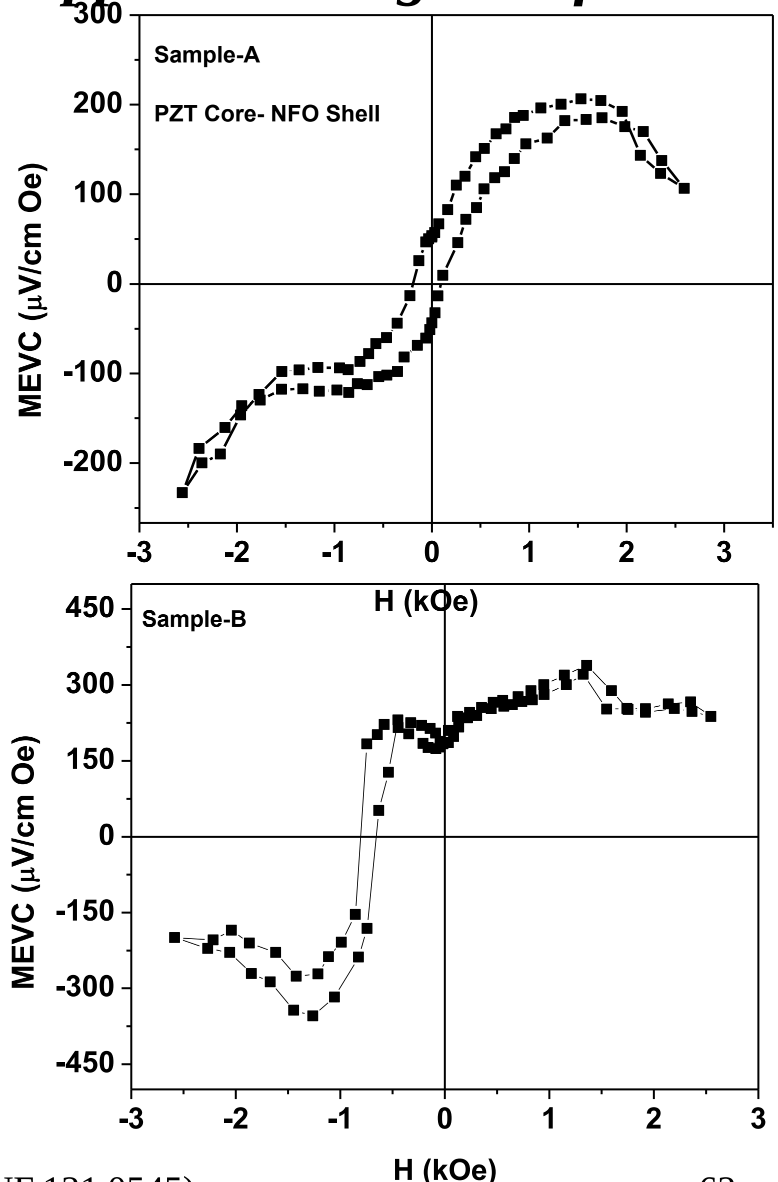
Magnetostriction induced voltage in PZT measured in a film assembled in nonuniform H

ME voltage coefficient measured with a bias field and ac field parallel to sample plane

Induced voltage measured across the sample.

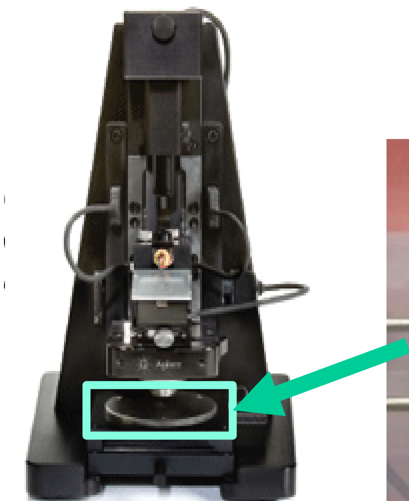
A very high MEVC for zero-bias field (evidence for a remnant magnetization that acts as bias field).

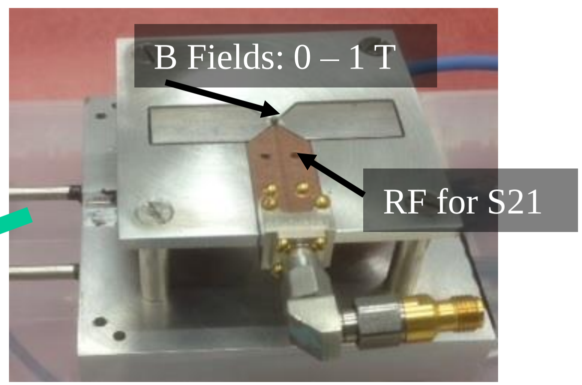
MEVC comparable to bulk composites and
 thick film samples.



Converse ME effects by E-tuning of FMR

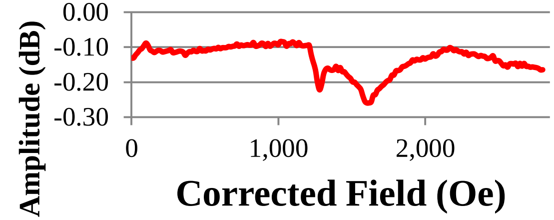
Scanning Microwave Microscopy – Modification for Magnetic and S_{11} Measurements



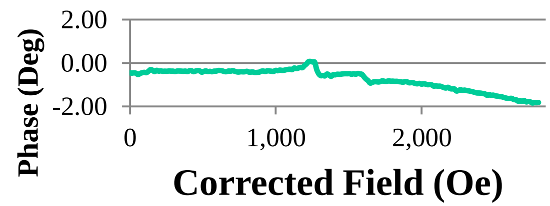


Calibrate magnetic field strength with a YIG film

YIG Film Amplitude S11 @ 6.25 GHz

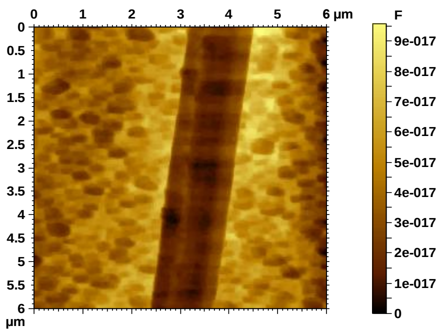


YIG Film Phase S11 @ 6.25 GHz

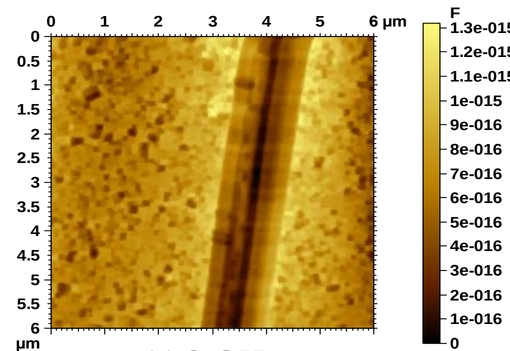


SMM of PZT/NFO Core-shell wires

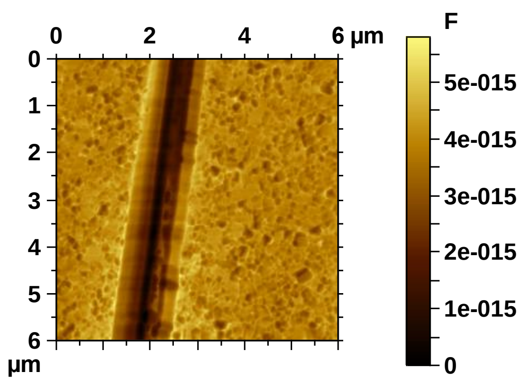
Capacitance (impedance) images over 2-20 GHz show well resolved core-shell structure for the fibers with PZT core and NFO shell.



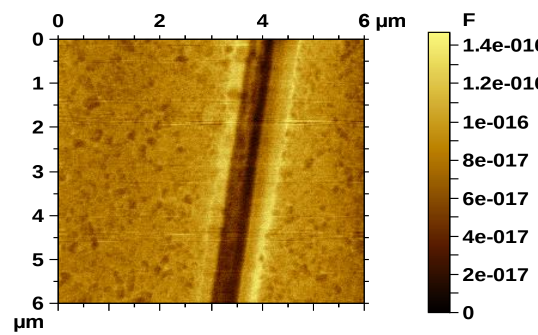
4.9 GHz



11.2 GHz



15.8 GHz

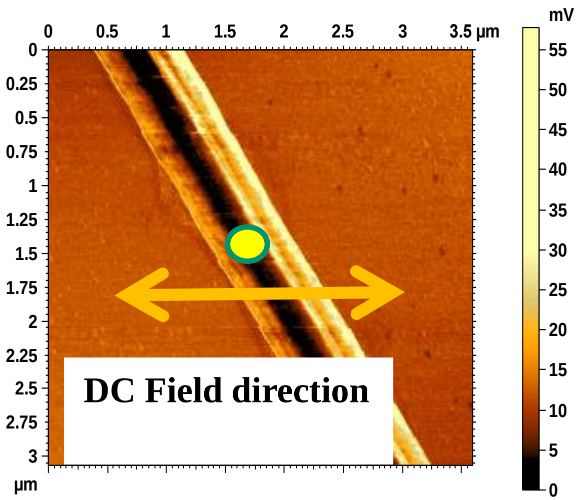


19.7 GHz

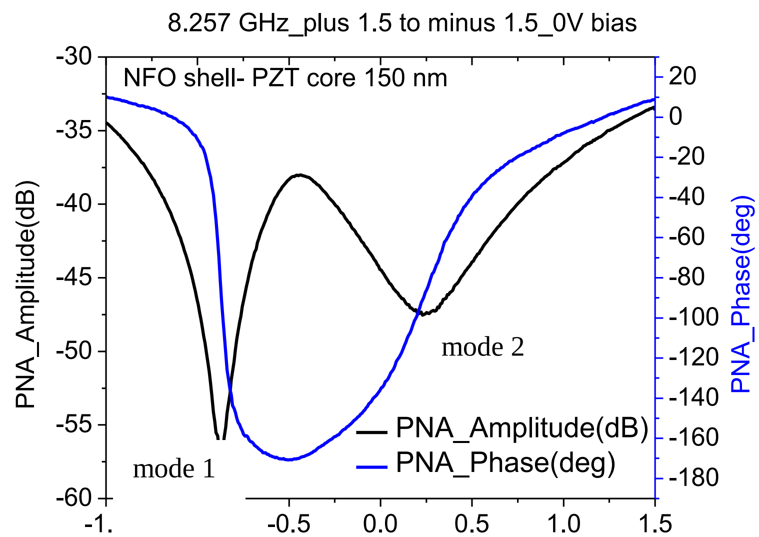
E-tuning of FMR in NFO (core)-PZT (shell) fiber

Measurement and Results

Amplitude of S_{11}



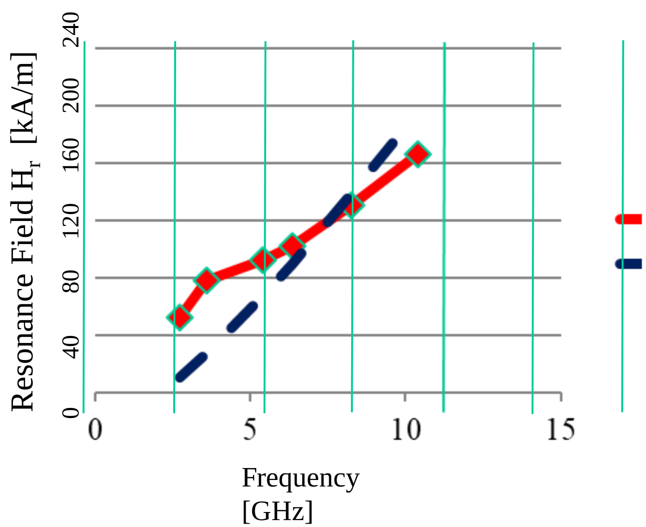
Field sweep at a constant frequency



1V ~ 160 kA/m

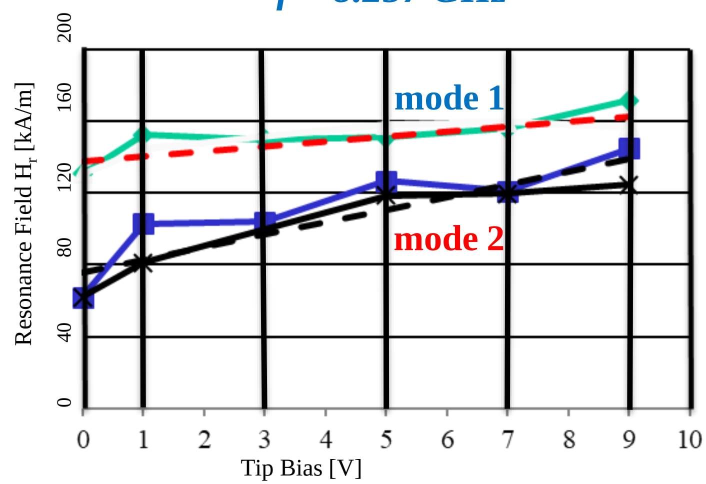
Measurements and Results

Resonance Field - Frequency Dependence



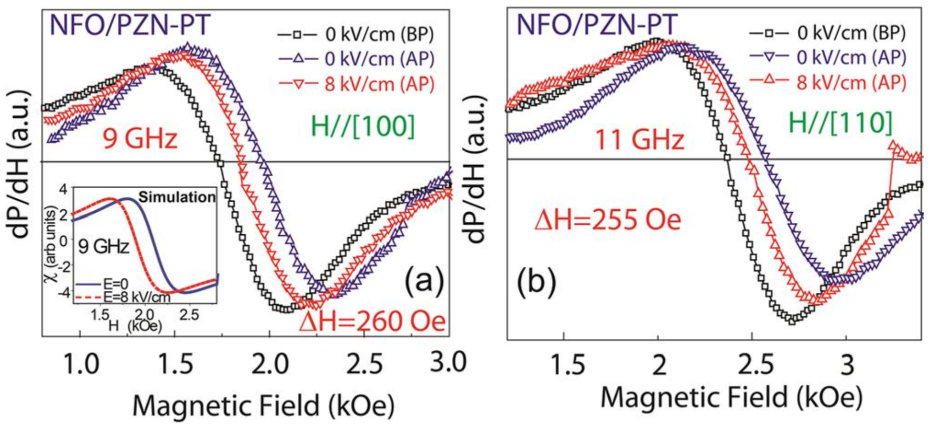
Solid line- experiment
Dashed line – theory

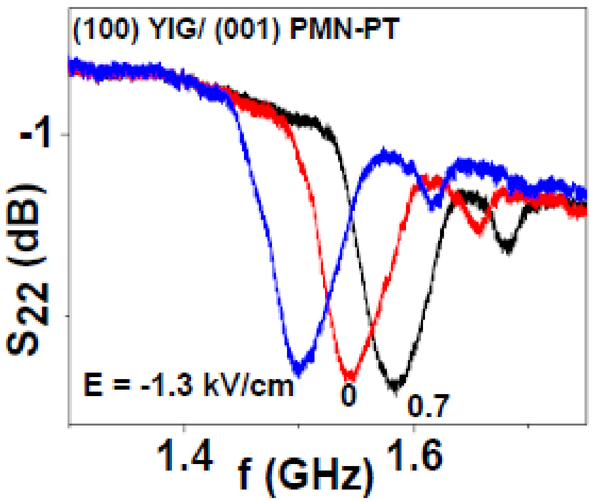
f = 8.257 GHz



Average ME coupling mode 1 : 2.75 kA/Vm
mode 2 : 7.08 kA/Vm

Comparison of ME coupling strength: Core-shell fibers vs thin films





ME coupling: 0.6 Oe/V (24 A/V m)

ME coupling: 0.3 Oe/V (13 A/V m)

Summary – Core-shell Nanowires

Ferrite-ferroelectric core-shell nanofibers were synthesized by electrospinning.

Fibers were assembled into superstructures in uniform or nonuniform magnetic fields.

ME effects studied by magnetic field induced polarization, magneto-dielectric effect, low-frequency ME effects and voltage tuning of FMR.

Results indicate strong ME coupling in the systems.